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AMERICAN INSTITUTE OF MINING
AND METALLURGICAL ENGINEERS
(INCORPORATED)

VOL. LXXIII

**CONTAINING PAPERS AND DISCUSSIONS PRESENTED AT MEETINGS
HELD IN NEW YORK, FEBRUARY, 1925; SALT LAKE CITY,
UTAH, SEPTEMBER, 1925; INSTITUTE OF METALS
DIVISION, SYRACUSE, N. Y., OCTOBER, 1925;
AND NEW YORK, FEBRUARY, 1926**

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AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS
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PREFACE

For many years the volumes of the TRANSACTIONS contained all the papers presented before the Institute during a year. As the number of papers read increased it became necessary to print more than one volume. In order to bring papers on the same or related subjects together they sometimes were segregated without reference to the year in which they were read. For example, Vol. LXII, published in 1920, contained the iron and steel papers read at meetings held in September, 1918, February, 1919, and September, 1919. Up to 1920, the Institute published a monthly *Bulletin* in which much material was printed that was not republished in the TRANSACTIONS. The *Bulletin* has been replaced by the magazine, MINING AND METALLURGY, which does not contain the full text of all papers presented before the Institute and does include much that does not go into the TRANSACTIONS. Papers, discussions and committee reports are also printed as pamphlets and circulated in that form. All papers in one or more major divisions of the field of work of the Institute are sent to members who request such service, and individual pamphlets on application.

The Institute has also published a number of special volumes, sometimes included among the TRANSACTIONS and sometimes not. Among such special volumes may be mentioned the Posepny and Emmons volumes on ore deposits, the Raymond Memorial volume and the pyrometry volume. The increased interest in petroleum technology led to a symposium on petroleum and gas at the February, 1924 meeting and the papers read were printed in a 264-page volume entitled, "Production of Petroleum in 1923." A similar volume was issued for 1924. Last year the papers presented covered not only production but production engineering, transportation, refining and petroleum economics and resulted in a volume of 784 pages which has been sent to all members who signified a desire for it.

There has been, through the years, a distinct drift toward special volumes. The Petroleum Division has developed to the stage where a separate volume best meets the needs of the Division. This is not sent to other members unless they so request. It seems probable that the other Divisions will eventually need similar service and only selected papers of value for permanent reference will be published in the TRANSACTIONS.

This volume contains the Howe Memorial Lecture, and the papers presented at the Salt Lake City Meeting, September, 1925, the Annual Meeting in New York, February, 1926, and the Institute of Metals Meeting at Syracuse, October, 1925, in the fields of non-metallic minerals, milling and concentration, non-ferrous metallurgy, iron and steel, and the Institute of Metals. Papers on mining methods, mine ventilation, coal and coke, and on mining geology read at these same meetings will appear in the next volume, which is being held to include papers on these subjects presented at the Pittsburgh meeting, October, 1926.

H. FOSTER BAIN.
Secretary

CONTENTS

	PAGE
PREFACE	iii
OFFICERS AND DIRECTORS	xi
TECHNICAL COMMITTEES	xii
NECROLOGY	xxviii
BIOGRAPHIES	xxix

PROCEEDINGS

Salt Lake City Meeting, 1925	xvii
Syracuse Meeting, 1925	xx
New York Meeting, 1926	xxi

PAPERS

Non-ferrous Metallurgy

Effect of Zinc Oxide on the Formation Temperatures of Some Ferrous Slags. By HORACE THARP MANN (With Discussion)	3
Recovery of Copper by Leaching, Ohio Copper Co. of Utah. By ARVID E. ANDERSON and FRANK K. CAMERON (With Discussion).	31
Leaching Mixed Copper Ores with Ferric Sulfate; Inspiration Copper Co. By G. D. VAN ARSDALE (With Discussion).	58
Production of Ferric Sulfate and Sulfuric Acid from Roaster Gas. By G. L. OLDRIGHT, H. E. KEYES and F. S. WARTMAN (With Discussion)	84
Conductivity of Electrolytes Used in the Electrolytic Separation of Silver and Gold. By F. F. COLCORD, E. F. KERN and J. J. MULLIGAN (With Discussion)	108
Improvements in the Series System of Electrolytic Copper Refining Recently Developed by the Nichols Copper Co. By M. H. MERRISS (With Discussion)	123
Anaconda Electrolytic White Lead. By R. G. BOWMAN	146
Lead Smelting in Utah. By B. L. SACKETT, CARLOS BARDWELL, SIMON JACOB- SON and N. H. JENSEN (With Discussion).	171
Chief Consolidated Volatilization Process and Mill. By G. H. WIGTON (With Discussion)	200

Milling and Concentration

Method of Unloading Ores and Coarse-crushing Practice at Magna Plant of Utah Copper Co. By B. E. MIX and L. M. BARKER (With Discussion).	212
Mechanism of Filtration. By ARTHUR W. HIXSON, LINCOLN T. WORK and ISAAC H. ODELL, JR. (With Discussion).	225
Classification in Witwatersrand Mills. By BENNETT R. BATES (With Dis- cussion).	239
An Investigation of Crushing Phenomena. By A. M. GAUDIN (With Discussion)	253

	Page
Chloridising Mill of the Standard Reduction Co. By H. P. ALLEN and Wm. C. MADGE (With Discussion)	317
Milling Practice at Midvale. By C. A. LEMKE	342
Effect of Cyanogen Compounds on Floatability of Pure Sulfide Minerals.-I. By E. L. TUCKER and R. E. HEAD (With Discussion)	354
Effect of Cyanogen Compounds on the Floatability of Pure Sulfide Minerals.-II. By E. L. TUCKER, J. F. GATES and R. E. HEAD	372

Non-metallic Minerals

Mining and Preparation of Eastern Molding Sands. By R. M. BIRD (With Discussion)	381
The Use of Standard Tests of Molding Sands. By H. RIES (With Discussion)	394
American Glass Sands, Their Properties and Preparation. By CHARLES R. FETTKKE (With Discussion)	398
Washing and Sizing Sand and Gravel. By EDMUND SHAW	424
Preparation and Use of Industrial Special Sands. By W. M. WEIGEL (With Discussion)	434
Borate Deposits Near Kramer, California. By HOYT STODDARD GALE	449

Institute of Metals

Mechanical Properties of the Aluminum-Copper-Silicon Alloy as Sand Cast and as Heat Treated. By SAMUEL DANIELS and D. M. WARNER	464
Effect of Reheating on the Al-Cu-Ni-Mg and the Al-Cu-Fe-Mg (Piston) Alloys. By SAMUEL DANIELS.	479
The Lead-antimony System and Hardening of Lead Alloys. By R. S. DEAN, LYALL ZICKRICK and F. C. NIX (With Discussion)	505
A Preliminary Study of Magnesium-base Alloys. By BRADLEY STOUGHTON and M. MIYAKE (With Discussion).	541
Equilibrium Relations in Aluminum-copper Alloys of High Purity. By E. H. DIX, JR., and H. H. RICHARDSON	560
Modification and Properties of Sand-cast Aluminum-silicon Alloys. By ROBERT S. ARCHER and L. W. KEMPF (With Discussion)	581
The Microstructure of Aluminum. By K. L. MEISSNER (With Discussion)	622
The Relation between Metallurgy and Atomic Structure. By PAUL D. FOOTE	628
Hardness of Copper, and Meyer's Analysis. By SAMUEL L. HOYT and T. R. SCHERMERHORN (With Discussion).	657
The Effect of Lead and Tin with Oxygen on the Conductivity and Ductility of Copper. By NORMAN B. PILLING and GEORGE P. HALLIWELL (With Discussion).	679
Exudations on Copper Castings. By W. H. BASSETT and J. C. BRADLEY (With Discussion)	700
Microscopic Structure of Copper. By H. B. PULSIFER (With Discussion)	707
Symposium on Gas in Copper	742
Embrittlement of Copper by Hot Reducing Gases. By T. S. FULLER (With Discussion; for discussion see also page 772).	744
Action of Reducing Gases on Heated Copper. By W. H. BASSETT and J. C. BRADLEY (With Discussion).	755
Annealing of Commercial Copper to Prevent Embrittlement by Reducing Gases. By SUSAN B. LEITER (With Discussion).	776
Estimation of Oxygen and Sulfur in Refined Copper. By W. H. BASSETT and H. A. BEDWORTH (With Discussion)	784

CONTENTS

vii

	PAGE
Special Nickel Brasses. By OLIVER SMALLEY	799
The Cracking of the Nickel Silvers in the Course of Annealing. By E. O. JONES and E. WHITEHEAD (With Discussion)	834
Amorphous Cement and the Formation of Ferrite in the Light of X-ray Evi- dence. By FRANCIS B. FOLEY (With Discussion)	850

Iron and Steel

The Current Theories of the Hardening of Steel Thirty Years Later. By ALBERT SAUVEUR (With Discussion)	859
An Introduction to Ultra-violet Metallography. By FRANCIS F. LUCAS (With Discussion)	909
The Effect of Annealing upon the Hardness of Cold-worked Ingot Iron. By CHARLES Y. CLAYTON	926
Influence of Temperature, Time and Rate of Cooling on Physical Properties of Carbon Steel.-II. By FRANCIS B. FOLEY, CHAS. Y. CLAYTON and W. E. REMMERS.	929
Effect of Air Gap in Explosion System on Production of Neumann Bands. By FRANCIS B. FOLEY and J. E. CRAWSHAW (With Discussion).	948
The Iron-tungsten System. By W. P. SYKES (With Discussion)	968
Probable Error in Blast-furnace Records and Calculations Therefrom. By T. T. READ (With Discussion).	1009
Making Rimmed Steel. CARL PEIRCE (With Discussion).	1026
Combustion in the Open-hearth Furnace with Special Reference to Automatic Control. By K. HUESSENER	1047
Elimination of Metalloids in the Basic Open-hearth Process. By J. L. KEATS and C. H. HERTY, JR.	1079
Chemical Equilibrium of Manganese, Carbon and Phosphorus in the Basic Open-hearth Process. By C. H. HERTY, JR. (With Discussion)	1107

Howe Memorial Lecture

Last Twenty-five Years in Metallography. By WILLIAM CAMPBELL	1135
--	------

Index

INDEX	1179
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PROCEEDINGS

Salt Lake City Meeting, 1925

THE 132nd meeting* of the Institute was held at Salt Lake City, Utah, Aug. 31 to Sept. 3. It was one of the largest meetings held outside of New York City; 470 members and guests registered and many more were present at the sessions.

Preliminary to the meeting the Petroleum Division held sessions at Casper, Wyoming, Aug. 28, 29 and 30. The program included an inspection tour of the Salt Creek oil field and a trip to Rawlins, Wyo., via Independence Rock on the Oregon Trail and the Lost Soldier and Wertz oil and gas fields.

The Annual Banquet was held at Hotel Utah, and was followed by a dance. W. Mont Ferry, president of the American Silver Producers' Association, presided at the banquet. The principal address was made by President J. V. W. Reynders. Governor George H. Dern of Utah, the second speaker, discussed the engineer in politics. Former Senator Charles S. Thomas also addressed the members.

The Utah section and the mine operators of Utah made the meeting a very pleasant one for the visiting members. Golf, swimming, motoring, dancing, luncheons, dinners and teas filled all the spare time. There were six field excursions by train and motor, the members visiting Bingham, Murray, Midvale, Ironton, Tintic, Park City and Tooele. Two hundred and forty took part in the trip to Bingham, where the Magna and Arthur plants of the Utah Copper Co. and the Garfield copper smelter of the American Smelting & Refining Co. were visited. This trip took the party to the open-cut workings of the former concern.

A party of members visited the lead smelter of the American Smelting & Refining Co. and that of the United States Smelting, Refining & Mining Co. at Murray, and inspected the concentration plant for complex ores and the arsenic recovery plant at Midvale.

Other trips took various groups of the members to the smelter of the Columbia Steel Corporation at Ironton, Utah; the silver-lead mines of the Tintic Standard, Chief Consolidated and other companies, and the silver-lead and silver-lead-zinc orebodies of Silver King Coalition, Ontario, Park City Mining & Smelting, Keystone, and the Park-Utah companies, at Park City. To those who took the Park City trip luncheon was served underground at the Silver King Coalition mines.

Luncheon was served at the International smelter to those who visited Tooele. A feature of this trip was the opportunity afforded to observe

* For news story of meeting see MINING AND METALLURGY, (Oct., 1925) 508.

the treatment of complex custom ores for the separation of lead, zinc and iron contents by differential flotation.

On the evening of Sept. 4, two small parties were organized, one to visit the parks of Southern Utah and the other Yellowstone Park.

The lot of the visiting ladies at the meeting was made pleasant by luncheons at the Country Club, motor driving, and a special reception at Hotel Utah, and by other entertainment arranged by the Woman's Auxiliary.

TECHNICAL SESSIONS

Milling and Concentration

L. S. CATES, Chairman

Tintic Standard Co.'s Mill. H. P. ALLEN and W. C. MADGE

Flotation Development and Simplification at the Ophir Hill Consolidated Mill.

CARL A. LEMKE

Method of Unloading Ores and Coarse Crushing Practice at Magna Plant of Utah Copper Co. B. E. MIX and L. M. BARKER

Effect of Cyanogen Compounds on Floatability of Pure Sulfide Minerals. I. E. L. TUCKER and R. E. HEAD.

Mining and Geology

JAMES W. WADE, Chairman

Tintic Standard Mine. JAMES W. WADE

Leaching in Place at Ohio Copper Co.'s Mine. ARVID E. ANDERSON

Ore Deposits and Their Relation to Structural Geology. J. J. BEESON

Electric Shot Firing Experiments in Coal Mines. A. C. WATTS

G. W. CRANE, Chairman

Deep Hole Prospecting at Chief Consolidated Mine. CHARLES DOBBEL

Shovel Operations at Bingham Utah Copper Co. H. C. GOODRICH

Notes on Geology of Tintic District. G. W. CRANE

Iron Fields of the Iron Springs and Pinto District, Iron County, Utah. DUNCAN MAC VICHIE

Ore Occurrences of the Park City District. FORREST MATHEZ

Metallurgy

A. B. YOUNG, Chairman

New Byproduct Coke Plant of the Columbia Steel Corporation. C. T. KEIGLEY

Blast Furnace Plant of the Columbia Steel Corporation. P. W. JACKSON

Application of Cottrell Process in Lead and Copper Smelting. A. L. LABBE

The Development of Differential Flotation on Complex Sulfide Ores. LIONEL BOOTH

W. W. NORTON, Chairman

The Use of Pulverized Coal in Copper Refining Furnaces. ROY S. MILLER and E. S. BARDWELL

Use of Pulverized Fuel. H. J. SAVAGE

Chief Consolidated Volatilization Plant. G. W. WIGTON

Lead Smelting in Utah. B. L. SACKETT, CARLOS BARDWELL, SIMON JACOBSON and N. H. JENSEN

Evolution in the Preparation of Ores for Lead Blast Furnaces. D. W. JESSUP

Anaconda Electrolytic White Lead. R. G. BOWMAN. Production of Ferric Sulfate and Sulfuric Acid from Roaster Gas. G. L. OLDRIGHT, H. E. KEYES and F. S. WATMAN.

Petroleum

[Casper Meeting, Aug. 29 and 30]

F. JULIUS FOHS, Chairman

Sketch of Geology and Formations of Central Wyoming. J. G. BARTRAM

The Naval Oil Reserves. MAX W. BALL

Shutting in Rangely Gas Well. J. A. HOLMES

Lost Soldier Oil Field. E. W. KRAMPERT

The Billy Creek Field. W. H. GEIS

Problems of Pumping Deep Wells. L. C. UREN.

Core Drilling in Geologic Exploration as Applied in Wyoming and Montana. J. G. BARTRAM and J. H. WILSON

Graphic Method of Work Done by Producing Wells. J. C. LINDSAY

Drilling Wildcat Wells in Wyoming. E. G. SINCLAIR

Cleaning Oil Wells by Compressed Air. A. A. BEARD and R. A. BONNEL

Use of Gas Meters for Determination of Pay Strata in Oil Sands. C. V. MILLIKAN

Cleaning Oil Wells by Heated Oil. W. J. KNOX

Application of Mining Tax Laws to the Petroleum Industry. M. O. DANFORD

SALT CREEK FIELD SYMPOSIUM

History of Production of Salt Creek Field. E. L. ESTABROOK and C. M. RADER
Discussion:

G. O. SMITH, W. H. GEIS, A. W. PEAKE, D. B. DOW

Water Shut-off Methods in the Salt Creek Field. R. O. ARMSTRONG and C. M. RADER

Waters of the Salt Creek Field. H. W. YOUNG and E. L. ESTABROOK

Institute of Metals Division Meeting

THE annual joint meeting* of the Institute of Metals Division and the American Foundrymen's Association was held at Syracuse, N. Y., Oct. 5-9. The registration was about 150. A feature of the meeting was the Round Table discussion at which 80 members, divided into groups, discussed a number of pertinent subjects. The following papers were presented:

Notes on the Fatigue of Non-ferrous Metals. H. F. MOORE

Endurance Properties of Non-ferrous Metals. D. J. MCADAM, JR.

The Cracking of the Nickel Silvers in the Course of Annealing. E. O. JONES and E. WHITEHEAD

Special Nickel Brasses. OLIVER SMALLEY

Amorphous Cement and the Formation of Ferrite in the Light of X-ray Evidence. FRANCIS B. FOLEY

Mechanical Properties of the Aluminum-copper-silicon Alloy as Sand Cast and as Heat Treated. SAMUEL DANIELS and D. M. WARNER

* For news story of meeting see MINING AND METALLURGY, (Nov., 1925) 570.

New York Meeting

THE 133rd meeting* of the American Institute of Mining and Metallurgical Engineers was held at New York, Feb. 15 to 18, 1926, with a total registration of approximately 1300.

Prof. William Campbell, of the School of Mines, Columbia University, New York, delivered the Henry M. Howe Memorial lecture. The title of his lecture was "Twenty-five Years in Metallography."

Paul D. Foote, U. S. Bureau of Standards, Washington, D. C., delivered the annual lecture of the Institute of Metals Division. The title of his lecture was "The Relation between Metallurgy and Atomic Structure."

Aside from business and distinctly social gatherings there were in all 26 technical sessions, two formal lectures, three group luncheons, four group dinners, and numerous small conferences and committee meetings. The Petroleum Division led with seven technical sessions. The Institute of Metals Division held four sessions, gave a dinner, and presented the Howe lecture by Prof. Campbell. The Mining Methods Committee held two sessions and a luncheon; the Coal and Coke Committee, two sessions; the Milling Methods Committee, one session and a dinner; the Industrial Relations Committee, the same; Mine Ventilation Committee, two sessions, and the Non-ferrous Metallurgy, Non-metallic Minerals, Mining Geology and Ground Movement and Subsidence committees, one each. The Committee on Education met at a well-attended luncheon.

At the annual business meeting on Feb. 16, the following ticket was elected, and the reports of the President, Treasurer and Secretary were presented:

Samuel A. Taylor, Director and President; B. O. Mahaffey, Director and Vice-President; Carl A. Meissner, Director and Vice-President; L. K. Armstrong, Director; W. Spencer Hutchinson, Director; H. A. Guess, Director; Seeley W. Mudd, Director; Reno H. Sales, Director.

E. De Golyer was elected First Vice-President; Charles F. Rand, Treasurer; H. Foster Bain, Secretary, and T. T. Read, Assistant Secretary, at the meeting of the Directors on Tuesday evening.

The Section Representatives held two sessions on Monday morning and afternoon, respectively, at which written reports were submitted by each division, and the representatives enlarged orally upon the chief points in their reports. President S. A. Taylor presided.

* For news story of meeting see MINING AND METALLURGY, (March, 1926) 105.

The Woman's Auxiliary held their annual meeting on Tuesday morning and afternoon. Various features of general interest and entertainment for each day that the Institute met characterized the program for the ladies.

A joint session of the Metropolitan sections of the American Society of Civil Engineers, the American Institute of Mining and Metallurgical Engineers, the American Society of Mechanical Engineers and the American Institute of Electrical Engineers was held on Thursday evening, Feb. 18, in the Auditorium. The topic discussed was "The Effect of the Diesel Electric Locomotive on the Problem of Railroad Electrification."

A buffet luncheon was served each noon at the Institute Headquarters. These luncheons were largely attended by members of the Institute, their guests and the members of the Woman's Auxiliary.

The Annual Smoker was held in the banquet hall of Mecca Temple, on Monday evening.

The Annual Dinner-dance was held at the Waldorf-Astoria on Wednesday evening. It was attended by 607 members and guests. The President's Reception preceded the dinner. At the latter Wilbur A. Nelson presided as toastmaster. The James Douglas gold medal was presented to James M. Callow. The Robert W. Hunt medal was presented to Charles L. Kinney, Jr. Announcement was made of the award of the J. E. Johnson, Jr., prize to S. P. Kinney. Addresses were made by J. V. W. Reynders, retiring President; S. A. Taylor, President of the Institute; G. S. Davison, President of the American Society of Civil Engineers; Scott Turner, Director of the Bureau of Mines; H. Foster Bain, Secretary of the Institute, and T. C. Denis, the latter responding for the Canadian Mining Institute.

The annual excursion on Feb. 18, was a sightseeing expedition by motor car to Bear Mountain. The members crossed the new Bear Mountain Bridge on foot, closely examining the beautiful structure, and after luncheon at Bear Mountain Inn, J. V. W. Reynders spoke briefly of some of the engineering difficulties encountered in the construction of the bridge.

Through the courtesy of Ole Singstad, chief engineer of The Holland Tunnel, two parties of members were conducted through the tunnel and its ventilation and other engineering features were explained to them.

TECHNICAL SESSIONS

Petroleum

GENERAL SESSION

F. JULIUS FOHS, Chairman

World Production of Petroleum in 1925. E. L. DE GOLYER
Taxation and the Oil Industry. A. D. BROKAW

Technologic Progress in the Oil Industry. F. JULIUS FOHS
Research and the Oil Industry. DR. VAN. H. MANNING

PRODUCTION ENGINEERING SYMPOSIUM

F. JULIUS FOHS, Chairman

Spacing of Oil Wells. FRANK M. BREWSTER

Core Drilling Technology:

1. Diamond Drills. R. D. LONGYEAR and P. W. DONGVAN

2. Special Type Drills. J. E. ELLIOTT

3. Basket Cores. E. CALL BROWN

Increasing Production by Shooting. H. B. HILL

Increasing the Extraction of Oil by Water Flooding. JOSEPH B. UMPLEBY

REFINING SYMPOSIUM

DR. T. G. DELBRIDGE and DR. C. H. OSMOND, Chairmen

Factors Affecting the Cracking of Petroleum. CHARLES L. PARMELEE

Discussion:

Cross Process. DR. ROY CROSS

Dubbs Process. DR. GUSTAV EGLOFF

The Gasoline Problem. R. C. HOLMES

Jenkins Process. L. H. WELLING

Comparative Value, as Motor Fuel, of Cracked Gasoline vs. Straight Run Gasoline.

ARTHUR E. WELLS

Economic Incidence of Cracking. BENJAMIN T. BROOKS, ROLAND B. DAY,
ARTHUR KNAPP

Basic Changes in Refining Processes. WALTER MILLER

Special Discussions:

A. Distillation by Pipe Stills. J. A. PRIMROSE

B. Fractionation. W. A. PETERS, JR.

C. Treating. A. E. MILLER

Liquid Sulfur Dioxide Process. DR. L. EDELEANU

D. Wax Separation. MAX B. MILLER

E. Economic Effect of Basic Changes in Refinery Operation. WALTER MILLER

Anti-knock Gasolines and Special Engine Development. DR. S. W. SPARROW

Discussion:

Economic Effect of the Anti-knock Motor Fuels. A. L. CLAYDEN, H. L.
HORNING

TRANSPORTATION SYMPOSIUM

DOUGLAS S. BUSHNELL, Chairman

Transportation of Petroleum. CHARLES FITZGERALD

Evaporation Losses in Storage and Transportation. J. H. WIGGINS

An Investigation into the Cause of Breakage in Crude Pipe Line Transportation Systems. NELSON B. DELAVAN

Corrosion of Pipe Lines and Protective Covering. F. RAY MCGREW

PRODUCTION SYMPOSIUM

DR. JAMES H. GARDNER, Chairman

Review of American Production. F. JULIUS FOHS
California. G. C. GESTER and E. W. WAGY

Kansas-Oklahoma. BURR McWHIRT

Gulf Coast. LOUIS FREEDMAN

Texas, Outside Gulf Coast. DR. F. H. LAHEE

Arkansas and Louisiana. D. T. RING

Rocky Mountain District. FRED E. WOOD

Appalachian Fields. GEORGE TURNBULL

Mississippi Valley Fields. GAIL F. MOULTON, HUGH D. MISER and W. N. LOGAN

Alaska. P. S. SMITH

Mexican Oil Fields. VALENTIN R. GARFIAS and R. V. WHETSEL

Venezuela and the West Indies. EDWIN B. HOPKINS and H. J. WASSON

Colombia and Peru. L. G. HUNTLEY

Argentina. F. T. OSTRANDER

Russia. BASIL B. ZAVOICO

Near East. E. L. PORCH, JR.

Australasia. F. G. CLAPP

Suggested Nomenclature and Correlation of the Geological Formations in Venezuela.

A. HAMILTON GARNER

Possibilities of Future Production from the Pre-Chattanooga Series of Northeastern

Oklahoma. LUTHER H. WHITE

PETROLEUM ECONOMICS SYMPOSIUM

F. JULIUS FOHS, Chairman

Petroleum Statistics and the Economic Situation. ARTHUR KNAPP

The Relation between Price and Stocks of Gasoline. JOSEPH E. POGUE

Forecasting Petroleum Production. J. MELVILLE SANDS and C. CAMPBELL OSBORN

Discussion by JOSEPH E. POGUE

The Trend of Prices in the Petroleum Industry. JOSEPH E. POGUE

Some Economic Aspects of the Community Oil Lease FAY WRIGHT

MINING METHODS

Mining Petroleum in France and Germany. GEORGE S. RICE and J. A. DAVIS

The Ranney Process of Mining Oil. LEO RANNEY

Mine Ventilation Committee

GEORGE S. RICE, Chairman

Address by the Chairman

Operating Characteristics of Centrifugal Fans and Use of Fan Performance Curve.

LOUIS W. HUBER

Theoretical Rating Compared with Operating Performance of Centrifugal Mine Ventilating Fans. A. S. RICHARDSON

Economic Design of Mine Airways. A. S. RICHARDSON

The Holland Tunnel. OLE SINGSTAD

Permissible Limits of Toxic and Noxious Gases in Mine and Tunnel Ventilation.

R. R. SAYERS

Discussion of Theory of Mine Ventilation. Presented by A. C. CALLEN

Some Important Factors in Metal Mine Ventilation. G. E. McELROY

Report of Sub-committee on Coal Mine Ventilation. FRANK HAAS

Non-ferrous Metallurgy

E. P. MATHEWSON, Chairman

Improvements in the Series System of Electrolytic Copper Refining Recently Developed by the Nichols Copper Co. M. H. MERRISS

The Conductivity of Electrolytes Used in the Electrolytic Separation of Silver and Gold. F. F. COLCORD, E. F. KERN and J. J. MULLIGAN

Leaching Mixed Copper Ores with Ferric Sulfate; Inspiration Copper Co. G. D. VAN ARSDALE

Effect of Zinc Oxide on the Formation Temperatures of Some Ferrous Slags. HORACE THARP MANN

Treatment of the Telluride-bearing Gold Ores of the Wright-Hargreaves Mines, Ltd. W. A. MUELLER, J. E. GRANT and C. L. HEATH

Milling and Concentration

GALEN H. CLEVINGER, Chairman

Mechanism of Filtration. ARTHUR W. HIXSON, LINCOLN T. WORK and ISAAC H ODELL, JR.

Classification in Witwatersrand Mills. BENNETT R. BATES

An Investigation of Crushing Phenomena. A. M. GAUDIN

Non-metallic Minerals

DR. H. RIES, Chairman

Mining and Preparation of Eastern Molding Sands. R. M. BIRD

The Use of Standard Tests of Molding Sands. H. RIES

American Glass Sands, Their Properties and Preparation. CHARLES R. FETTKE

Washing and Sizing Sand and Gravel. EDMUND SHAW

Preparation and Use of Industrial Special Sands. W. M. WEIGEL

Pyro- and Hydro-treatment of Magnesite and Dolomite. HUGH M. HENTON

Borate Deposits Near Kramer, California. HOYT STODDARD GALE

Institute of Metals Division

A. E. WHITE, Chairman

Effect of Reheating upon the Al-Cu-Ni-Mg and the Al-Cu-Fe-Mg (Piston) Alloys.

SAMUEL DANIELS

Endurance Properties of Non-ferrous Metals—II. D. J. McADAM, JR.

The Lead Antimony System and the Hardening of Lead Alloys. R. S. DEAN, L. ZICKRICK and F. C. NIX

A Preliminary Study of Magnesium Base Alloys. BRADLEY STOUGHTON and M. MIYAKE

DR. ZAY JEFFRIES, Chairman

Equilibrium Relations in Aluminum-copper Alloys of High Purity. E. H. DIX, JR., and H. H. RICHARDSON

Modification and Properties of Sand-cast Aluminum-silicon Alloys. ROBERT S. ARCHER and L. W. KEMPF

The Microstructure of Aluminum. K. L. MEISSNER

SAMUEL A. TAYLOR, Chairman

Relation between Metallurgy and Atomic Structure. PAUL D. FOOTE

C. S. WITHERELL, Chairman

- The Hardness of Copper. SAMUEL L. HOYT and T. R. SCHERMERHORN
 The Effect of Lead and Tin with Oxygen on the Conductivity and Ductility of Copper.
 NORMAN B. PILLING and GEORGE P. HALLIWELL
 Exudations on Copper Castings. W. H. BASSETT and J. C. BRADLEY
 The Microscopical Structure of Copper. H. B. PULSIFER

S. SKOWRONSKI, Chairman

- Some Examples of Copper Made Brittle by Hot Reducing Gases. T. S. FULLER
 Action of Reducing Gases on Heated Copper. W. H. BASSETT and J. C. BRADLEY
 The Annealing of Commercial Copper to Prevent Embrittlement by Reducing Gases.
 S. B. LEITER
 The Estimation of Oxygen and Sulfur in Refined Copper. W. H. BASSETT and H. A.
 BEDWORTH

Mining Geology

E. F. BURCHARD, Chairman

- Magmas, Dikes and Veins. WALDEMAR LINDGREN
 Geology of the Yoquivo, Chihuahua Mining District. C. W. HALL
 Geology and Ore Deposits of the Asientos-Tepezala District, Aguascalientes, Mexico.
 G. E. ANDERSON
 Geology of the Zaruma Gold District of Ecuador. PAUL BILLINGSLEY
 Lead and Zinc in Eastern Canada. FREDERICK J. ALCOCK
 Electrical and Electromagnetic Prospecting. HANS LUNDBERG
 Ore Deposition and Enrichment at the Magma Mine, Superior, Arizona. M. N.
 SHORT and I. A. ETTLINGER

Iron and Steel

DR. J. A. MATHEWS, Chairman

- The Current Theories of the Hardening of Steel Thirty Years Later. ALBERT
 SAUVEUR
 A Photomicrographic Study of the Process of Re-crystallization in Certain Cold
 Worked Metals. VSEVOLOD N. KRIVOBOK
 A Process for the Prevention of Embrittlement in Malleable Cast-iron. L. H. MARSH-
 ALL
 An Introduction to Ultra-violet Metallography. FRANCIS F. LUCAS
 The Effect of Annealing upon the Hardness of Cold-worked Ingot Iron. CHARLES Y.
 CLAYTON

BRADLEY STOUGHTON, Chairman

- Influence of Temperature, Time and Rate of Cooling on Physical Properties of Car-
 bon Steel.—II. FRANCIS B. FOLEY, CHARLES Y. CLAYTON and W. E. REMMERS
 Effect of Air Gap in Explosion System on Production of Neumann Bands. FRANCIS
 B. FOLEY and J. E. CRAWSHAW
 The Iron-tungsten System. W. P. SYKES
 Delta Iron in the Iron Chromium Alloys. E. C. BAIN
 Economic Significance of Cyanide Accumulation in the Blast Furnace. RICHARD
 FRANCHOT

OPEN HEARTH

J. V. W. REYNOLDERS, Chairman

- Making Rimmed Steel. CARL PEIRCE
 Combustion in the Open-hearth Furnace with Special Reference to Automatic Control.
 K. HUESSENER

Elimination of Metalloids in the Basic Open-hearth Process. J. L. KEATS and C. H. HERTY, JR.

Chemical Equilibrium of Manganese, Carbon and Phosphorus in the Basic Open-hearth Process. C. H. HERTY, JR.

Howe Memorial Lecture

J. V. W. REYNDERS, Chairman

Twenty-five Years of Metallography. WILLIAM CAMPBELL

Coal and Coke Symposium

CHESTER M. LINGLE, Chairman

Report of Coal and Coke Committee. Presented by H. N. EAVENSON

Data on Use of Loading Machine in Bituminous Mines. GRAHAM BRIGHT

Evaluation of Coal. R. H. SWEETSER

Air Sand Process of Cleaning Coal. THOMAS FRASER and H. F. YANCY

Relation of Origin and State of Carbonization of Coal to Problems of Low-temperature Carbonization. S. W. PARR

R. H. SWEETSER, Chairman

The Mt. Union Sand-flotation Plant for the Preparation of Bituminous Coal. T. M. CHANCE

Relation of Ash Composition to the Uses of Coal. A. C. FIELDNER and W. A. SELVIG

Explosibility of Coal and Other Dusts in a Laboratory Steel Dust Gallery. V. C. ALLISON

The Selection of Coals for the Manufacture of Coke. H. J. ROSE

*Mining Methods**

R. M. RAYMOND, Chairman

Top Slicing in Old Fills at El Bordo Mine, Mexico. R. J. MECHIN

Mining Methods in Grass Valley District, California. J. A. FULTON and A. B. FOOTE

Sharpening and Handling Drill Steels at Franklin. C. M. HAIGHT

SYMPOSIUM ON EXPLOSIVES

Some Drilling and Blasting Methods for Mining Coal in the United States. THEODORE MARVIN

Liquid Oxygen as an Explosive. FREDERICK W. O'NEIL and HERMAN VAN FLEET

Industrial Relations

C. E. DODGE, Chairman

The Organization of Industry. GEORGE E. ROBERTS

Employee Ownership in Industry. J. M. SHAW

Ground Movement and Subsidence

H. G. MOULTON, Chairman

Report of Subcommittee on Coal Mining to Committee on Ground Movement and Subsidence. Presented by H. N. EAVENSON

Subsidence Around a Salt Well. C. M. YOUNG

* See also Mining Methods, Petroleum Division, page xxiv.

Necrology

The following is a list of members who died in 1925. It is compiled from reports to the Secretary's office.

YEAR OF ELECTION	NAME	DATE OF DEATH	YEAR OF ELECTION	NAME	DATE OF DEATH
1920	ADAMS, CUYLER C.	May	1880	HUNT, F. F.	Apr. 10
1917	ALDER, ALFRED	Sept. 11	1902	KEHLER, CHARLES R.	Apr. 28
1916	BABCOCK, E. J.	Sept. 3	1917	KELLY, CHARLES BRACE	Sept. 20
1918	BACKERT, A. O.	Apr. 24	1923	KEMMERER, MAHLON S.	Dec. 29
1922	BITTNER, LOUIS J.	May 31	1911	KIDDIE, JOHN	Apr. 17
1923	BRACE, CHARLES LORING, JR.	May 2	1917	LEONARD, ALBERT	May 4
1898	BRINELL, J. A.	Nov. 17	1891	McCORMACK, G. B.	Nov. 28
1916	BRINGS, HENRY	Sept. 22	1905	MERRIMAN, MANSFIELD	June 7
1900	BROWN, CONY T.	Jan. 15	1902	MESTA, GEORGE	Apr. 22
1918	BUCHANAN, C. G.	Apr. 9	1903	MILLER, WILLET G.	Feb. 10
1916	BYERS, WHEATON BRADISH	May. 7	1916	MOLINO, OLEGARIO	Apr. 28
1890	CHANDLER, CHAS. F.	Aug. 26	1907	NAKAMURA, KEIJIRO	Jan. 2
1882	CLARK, W. A.	Mar. 2	1920	NEEL, HIRAM A.	Feb. 18
1911	CRABTREE, FRED	Feb. 14	1900	OSBORNE, FRANCIS D.	May 19
1880	CROCKER, A. L.	Oct. 21	1905	PEARSON, WILLIAM B.	Nov. 18
1921	CRONIN, JAMES	Mar.	1921	PECK, FREDERICK B.	Nov. 2
1903	CROSBY, WILLIAM O.		1911	PETTEBONE, EDGAR RICE	July 27
1904	DANIEL, W. B.		1891	REYNOLDS, GEORGE B.	Feb. 23
1901	DAVIS, STEWART A.	Nov. 6	1876	RILEY, LEWIS A.	Apr. 23
1887	DAY, DAVID T.	Apr. 15	1876	SANDERS, R. H.	Jan. 23
1902	DEFTY, W. E.	July 23	1879	SCAIFE, WILLIAM LUCIEN	
1893	EMMONS, N. H., 2d.	May 25	1883	SHOCKLEY, WILLIAM H.	May 26
1880	FARRELL, AUSTIN	Dec. 25	1914	TACKMANN, HENRY	Nov. 24
1905	FRAMES, MINETT E.		1879	THOMAS, EDWIN	
1921	GANNETT, ROGER W.	Nov.	1913	THOMPSON, J. FRANK	Jan. 10
1920	GLASS, ANDREW	Nov.	1907	UREN, W. J.	Nov. 6
1918	GOBELANGTON, C. A.	Feb. 25	1903	VALENTINE, MALVERN R.	Mar. 25
1921	GRAY, BUNDY M.	Mar. 21	1872	VAN ARSDALE, W. H.	Mar. 16
1919	GREENFIELD, RAY C.	Oct. 28	1923	VAN DER VEEN, R. W.	Mar.
1921	HAGGIN, EDWARD R.	Sept. 13	1919	VAN HORN, S. E.	May 1
1915	HANFORD, JABEZ B.	Sept. 25	1919	WARREN, WESLEY W.	Sept. 8
1919	HAMILTON, H. L.	Dec. 29	1894	WEINBERG, E. A.	Apr. 2
1873	HARDEN, E. B.	July 11	1882	WILES, EDWIN L.	Jan. 19
1882	HARDMAN, JOHN E.	Apr. 3	1881	WILEY, W. H.	May 2
1921	HARTUNG, HERBERT C.	Apr. 29	1882	WILLIAMS, BEN	Sept. 2
1918	HAYNES, ELWOOD	Apr. 13	1919	WOLF, J. H. G.	Dec. 19

Biographies

Biographical sketches have been published in Mining and Metallurgy as follows:

NAME	DATE OF DEATH	ISSUE 1925	PAGE
EARLE J. BABCOCK.....	Sept. 3, 1925	Dec.	623
A. O. BACKERT.....	April 24, 1925	June	304
CONY T. BROWN.....	Jan. 15, 1925	March	162
CHARLES GORDON BUCHANAN..	April 9, 1925	May	250
WHEATON BRADISH BYERS...	May 7, 1925	June	305
CHARLES F. CHANDLER.....	Aug. 26, 1925	Nov.	578
WILLIAM A. CLARK.....	March 2, 1925	April	206
FREDERICK CRABTREE...	Feb. 14, 1925	April	208
JAMES CRONIN.....	March 3, 1925	May	251
W. B. DANIEL.....	March	162
DAVID TALBOT DAY.....	April 15, 1925	June	302
NATHANIEL HENRY EMMONS. 2d	May 25, 1925	Nov.	579
ROY C. GREENFIELD.....	Oct. 28, 1925	Dec.	623
MANSFIELD MERRIMAN.....	June 7, 1925	July	353
GEORGE MESTA.....	April 22, 1925	June	305
WILLET GREEN MILLER.....	Feb. 10, 1925	March	160
FREDERICK B. PECK.....	Nov. 2, 1925	Dec.	623
EDGAR RICE PETTEBONE.....	July 27, 1925	Nov.	578
LEWIS ADAMS RILEY.....	April 23, 1925	June	305
J. FRANK THOMPSON.....	Jan. 10, 1925	July	353
WILLIAM HENRY VAN ARSDALE	March 16, 1925	June	304
EDWIN L. WILES.....	Jan. 19, 1925	April	207
WILLIAM HALSTED WILEY..	May 2, 1925	June	305
		1926	
A. L. CROCKER.....	Oct. 14, 1925	Jan.	33
AUSTIN FARRELL.....	Dec. 25, 1925	Feb.	88
HARRY L. HAMILTON.....	Dec. 29, 1925	Feb.	89
CHARLES RAYMOND KEHLER..	April 28, 1925	June	267
WILLIAM H. SHOCKLEY.....	May. 26, 1925	Feb.	87
WILLIAM J. UREN.....	Nov. 6, 1925	Jan.	33

PAPERS

Effect of Zinc Oxide on the Formation Temperatures of Some Ferrous Slags

BY HORACE THARP MANN, OKMULGEE, OKLA.

(New York Meeting, February, 1926)

A FEW years ago, it was generally thought that from 15 to 18 per cent. of zinc oxide was the upper limit of a workable lead blast-furnace slag. With slags above this zinc-oxide content, the furnaces gave so much trouble because of hearth, wall, and crucible accretions that the campaign was very short. The time lost in cleaning out the frozen furnaces, for it was seldom possible to blow them out, and blowing in was so great that it was considered uneconomical to attempt the running of high-zinc slags, even if this were metallurgically possible. It is true that there are references to one or two slags much higher in zinc than the foregoing,¹ but the average smelterman regarded these as freaks and not to be considered for regular furnace work.

One or two plants, notably the plant of the United States Smelting Co. at Canyon City, Colo., ran charges higher in zinc. At this plant, the zinc-oxide content of the charge was frequently 20 per cent. and higher but the slags from these furnaces seldom ran over 10 to 12 per cent. zinc oxide. The furnaces were run with a large volume of air under a relatively low pressure, a low smelting column, and a very hot top; as a result, a large amount of zinc was volatilized. Even with the low smelting column and hot top, accretions caused much trouble and barring down was a daily occurrence.

At the time most of the theories on lead blast-furnace work were promulgated or worked out, it was necessary to run a furnace with a cold top in order to avoid an excessive loss due to fines and fume. At the same time, the smelting conditions had to be such that the lead and silver would be reduced and would enter the bullion. The slag had to be liquid but the charge must not give excessive accretions either in the hearth or on the walls of the furnace. This forced the operators to run the furnaces with a comparatively low blast, which, in turn, caused a small fuel consumption per unit of time with the accompanying result of a low working temperature.

¹ Henry F. Collins: *Metallurgy of Lead*. Griffin & Co., London, 1910, 156 (slag No. 13).

The low temperature and the construction of the furnace necessitated slags and bullion that did not hold much material in solution; the cooling of the slag and bullion, after passing the tuyeres, would have caused excessive segregation, and this material would have soon formed accretions, which would have ended the furnace campaign. At the same time the carbon of the coke was depended on for all of the reduction. If metallic iron was needed for the decomposition of sulfides and silicates, it was obtained by reducing a portion of the iron oxides of the charge with carbon. As a result, when attempts were made to force the furnace, either a hot top developed or excessive reduction was obtained; the metallic-iron sows were evidence of the latter.

The introduction of pot roasting, and later of sinter roasting, removed much of the trouble. The lumped product of these roasters materially lowered the dust losses from the furnace. At the same time, the coarse material permitted a better penetration of the blast, thus giving more uniform smelting conditions over the entire furnace. This change, from fine to coarse material, also permitted better furnace regulation. As a result, the melted material entered the crucible with a much more uniform temperature and there was much less segregation.

The general installation of the Cottrell process and of bag houses aided in recovering, in a large measure, the losses due to dusting, hot tops, and roasting. With this accomplished, it became possible to roast or sinter any ore and to use a much stronger blast, with the attendant advantage of a higher smelting temperature. The siphon tap was enlarged, so that accretions could be readily removed. Metallic iron was generally added to the charge to aid the reduction, rather than attempt to balance conditions so that just the proper amount of iron would be reduced from the charge.

With the increase in the temperature of the smelting zone, slags with a higher formation temperature and a high running temperature could be made, a hotter crucible could be maintained, and the general working conditions much improved. If an occasional hot top developed it was not a serious matter. In fact, at one plant the furnaces are operated with hot tops.² As a result, the "type slags" of the older lead metallurgy, which had comparatively low working temperatures, have practically disappeared.

In a few localities, the metallurgists experimented with slags high in zinc; the lead ores there being fairly high in zinc that could not be separated readily, if at all, mechanically. Likewise, it was not considered advisable to erect a hydroelectrolytic zinc plant for the treatment of these high-zinc lead ores for the recovery of the zinc. In other plants, it was not considered advisable to use the electrolytic process on all the complex ores.

² Private communication to Prof. Carle R. Hayward.

In these localities, they have succeeded in making slags with a zinc-oxide content as high as 38 per cent. without serious furnace troubles.³ One plant made a slag having a zinc-oxide content of 20.9 per cent. for 6 months and other slags up to 33 per cent. zinc oxide for long enough periods to show that they were commercial slags.⁴ An American plant ran its furnaces for over eighteen months on charges that produced slags having a monthly average above 18 per cent. zinc oxide and one month they were over 24 per cent. zinc oxide.⁵ The composition of these slags is given in Table 1.

TABLE 1

Footnote Reference	Pb, Per Cent.	S, Per Cent.	Zn, Per Cent.	ZnO, Per Cent.	CaO, Per Cent.	Fe, Per Cent.	FeO, Per Cent.	SiO ₂ , Per Cent.	Al ₂ O ₃ , Per Cent.	MnO, Per Cent.
6	1.9	2.4		24.15	6.8	31.0		17.6	4.6	
7	3.0		29.2		5.2	34.1		16.5		
8	3.0		30.9		4.7	31.9		13.5		
9				33.3	8.9		20.3	18.4		5.1
10	1 to 2	2 to 3		31.8	9.0		20.3	18.3	5 to 6	4.9

ECONOMIC CONSIDERATIONS

A question which naturally arises at this point is, why is it desirable to make slags with such a high-zinc content from the standpoint of the value of their contained zinc? One of these slags contains 30 per cent. of zinc which, at \$0.05 per lb. gives to the zinc in a ton of slag a gross value of \$30. At the present time, the answer is purely an economic one. The market will absorb practically all of the lead that the mines of the world can produce at a price that permits profitable operations. The general tendency, taken over a number of years, is a falling off in

³ R. G. Hall: Smelting Practice at Namtu. *Eng. & Min. Jnl.-Pr.* (1923) **115**, 757.

⁴ O. A. Woodward and J. C. Hughes: Lead Smelting Practice at the Port Pirie Works of the Broken Hill Associated Smelters Pty. Ltd. *Aust. Inst. of Min. & Met.* (1922) New Series No. 47.

⁵ Private communication to Prof. Carle R. Hayward.

⁶ Private communication to Prof. Carle R. Hayward.

⁷ and ⁸ R. G. Hall: Smelting Practice at Namtu. *Eng. & Min. Jnl.-Pr.* (1923) **115**, 757.

⁹ O. H. Woodward and J. C. Hughes: Lead Smelting Practice at Port Pirie Works of the Broken Hill Associated Smelters Pty. Ltd. *Aust. Inst. of Mng. & Met.* (1922) New Series No. 47.

¹⁰ Gilbert Rigg: Roasting and Lead Smelting Practice at the Port Pirie Works of the Broken Hill Associated Smelters Pty. Ltd. *Inst. Mng. & Met.* (1920) **29**, 377.

the average lead content of ores, indicating that the consumptive demand is increasing more rapidly than production. This is not the case with zinc. The production of zinc is regulated entirely by the consumptive demand. Nothing shows this more plainly than the great fluctuations in the yearly production which in the United States in the last twelve years has increased from 181,000 to 607,000 metric tons.¹¹ Normally the United States produces about 25 per cent. of the world's supply, yet in two years, because of high prices, the production of this country nearly doubled, the high figure being equal to about 60 per cent. of the world's normal supply. This was done without the opening up of any considerable number of new mines of any great size. As soon as the demand decreased, production was curtailed and in 1921 was about 18 per cent. of the normal annual production for the world.

Such districts as Leadville, Butte, etc. have extensive deposits of low-grade zinc ores that can, and will, be worked whenever there is sufficient demand to make their treatment profitable. At present, the richer ores are being worked, the grade being regulated by the price of zinc. These low-grade ores cannot compete with the high-zinc pure ores of the large zinc-producing districts of the country. Many of the western mines that can make a concentrate containing 50 per cent. zinc or better could hardly compete with the mines of the Mississippi Valley and New Jersey if it were not for the silver that the western ores usually carry. Until these conditions change, one may expect complex ores of lead and zinc or of lead, silver, and zinc that cannot be separated by mechanical means, or where a hydroelectrolytic plant is not feasible, to be smelted for their lead-silver content provided that there are sufficient lead and silver to make operations profitable. Without doubt, some time these slags will be treated for their zinc and, at the same time, the iron will probably be extracted. Several processes have been patented for extracting the zinc from slags of this sort, but they have been unable to compete with mines producing desirable concentrates. Until such time as the mines are unable to produce high-grade products the low-grade products will be of little value.

PROBLEM

In this problem an attempt was made to determine the formation temperatures of ferrous slags, containing from none up to as high as 60 per cent. zinc oxide, over as great a variation in the percentages of silica, iron, and lime, as one would be apt to encounter in practical smelting of lead ores high in zinc. As there were four variables, few determinations were made that did not have a direct bearing on the limited field of this problem. To attempt to work out all of the possibilities would take

¹¹ Mineral Industry (1915) 24; (1922) 31, 741.

several years' time and the writer doubts if this work would be justified by the practical application of the problem.

The formation temperatures of the various slags were obtained by determining the temperature at which "seger cones" (made from the synthetic slags) became liquid, by means of a platinum-platinum 10 per cent. iridium thermocouple with a potentiometer, up to the temperature limit of the couple, and with a Scimatco optical pyrometer above this temperature. These cones were of the usual form, having an equilateral triangular base $\frac{3}{8}$ in. on a side and a height of 1 in. They weighed from 0.8 to 1.1 gm., depending on the composition.

The materials used for making the cones were crushed quartz as the source of silica, calcium carbonate as the source of lime, zinc oxide, ferrous oxide, and a 10 per cent. solution of dextrine in water. The silica was in the form of quartz crystals crushed to pass a 100-mesh Tyler standard screen having openings 0.147 mm. (0.0058 in.); an analysis of this material gave 99.90 SiO₂. In this work, the crushed quartz was considered as containing 100 per cent. silica. None of the slags contained over 38 per cent. silica so that the greatest possible error from this source is 0.038 per cent.

Calcium carbonate was used to furnish the lime (CaO). This calcium carbonate was a precipitated product containing 56.00 CaO which was equivalent to 99.96 CaCO₃. The principal impurities were 0.01 per cent. MgO and 0.005 per cent. of FeO. The use of calcium oxide was attempted, but this was impractical because the alkalinity of this substance destroyed the adhesive properties of any ordinary bonding material. To develop the natural bonding property of the calcium oxide, it was necessary to add a large excess of water to the slag mixture and allow this wet charge to stand for about 6 hr. and then evaporate the excess of water, or to keep the charge moistened for three or four days. Either method was objectionable because of the rapid oxidation of the wet ferrous oxide. It is possible to bond the lime with hot paraffin, but this is never resorted to unless absolutely necessary, because of the great inconvenience in working with the hot materials.

The zinc oxide was a precipitated material containing 80.28 per cent. Zn, which is equivalent to 99.93 per cent. ZnO; this was considered as pure.

The ferrous oxide contained 77.49 per cent. Fe, which is equivalent to 99.70 per cent. FeO and in this work was considered as pure ferrous oxide. This material was slightly magnetic probably because of the presence of both metallic iron and the magnetic oxide. If the magnetic properties had been due to either metallic iron or magnetite alone, the analysis would have been higher or lower, depending on which was present. This was not considered a serious defect, for lead blast-furnace charges usually have both metallic iron and the higher oxides of iron in

them. It made the synthetic slags resemble actual conditions more closely.

The proportions for each slag were weighed to the nearest 0.1 mg. when the amount was 500 mg. or less and to the nearest milligram for quantities in excess of 500 mg. The total weight taken for each slag was between 5 and 10 gm. The dry materials were placed on a watch glass and thoroughly mixed with a spatula. This charge was then moistened with a 10 per cent. solution of dextrine in water to a consistency similar to that of glazier's putty. The incorporation of the bond required a thorough mixing and working so that each charge was mixed twice. No attempt was made to determine the percentage of solution necessary to give the correct consistency to the plastic material. Silica and ferrous oxide required a much smaller quantity of solution than calcium carbonate and zinc oxide. The total solution required varied for each slag. With pure iron silicates, it was difficult to get the proper consistency: one drop of solution in a 5-gm. charge made it too dry to work or too wet to mold. Any person making up a series of cones will find it much simpler to determine the quantity of solution required by a few preliminary trials than to determine the factors and calculate it for each slag. If the individual charges are of any appreciable size, however, it would be advisable to determine the moisture factor; but for charges of 10 gm. and under it is easier and quicker to determine the proper moisture content by the way the material feels when worked with a spatula.

The wet material was pressed into a seger cone mold, which had been coated with a thin film of oil. The cones were removed from the mold and placed on an oiled glass plate to dry. No trouble was experienced in removing the cones from the mold if it had been oiled and the material was not too wet.

It was found that dry glass was not suitable to receive the cones, as they stuck to the glass and, when drying, frequently cracked, or else were broken in their removal. The higher the iron content of the slag, the greater was the difficulty resulting from the cones sticking to the glass plate.

Furnace

The furnace used was a gas-fired muffle furnace. The combustion chamber was 14 in. wide by 14 in. high by 15 in. deep. This chamber was lined with a kaolin brick "KO" obtained from the Babcock & Wilcox Co., East Liverpool, Ohio. The gas ports and flue were lined with a bauxite brick, obtained from the same company. The top of the combustion chamber was carborundum tile. Two courses of brick were placed outside the lining, the first being of firebrick and the second an insulating brick. The burner was a Maxon Premix No. 1 with a water-cooled nozzle. The muffle was of carborundum 6½ in. wide by 4½ in.

high by $12\frac{1}{2}$ in. deep, inside. It was supported at the front on a bauxite brick and at the back by a "refrax" brick. Refrax bricks were used for baffles to distribute the gas. The position of the baffles was changed until the desired heat distribution was obtained. As this changes for

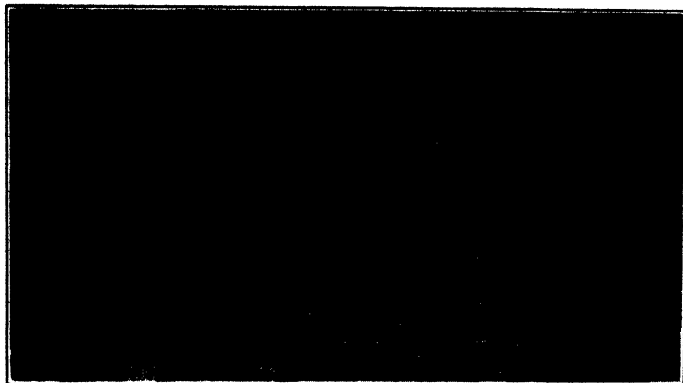


FIG. 1.—FURNACE CLOSED.

each design, no attempt was made to locate the position of these exactly on the drawings. With this furnace and burner, it was possible to get 1600° C. in the muffle. The writer several times heated firebrick until they were plastic. The method and details of construction are shown in Figs. 1 to 6.

The cones for the melting tests were mounted on a $\frac{1}{4}$ -in. layer of 80-mesh carborundum spread on a piece of high melting-point fireclay brick.

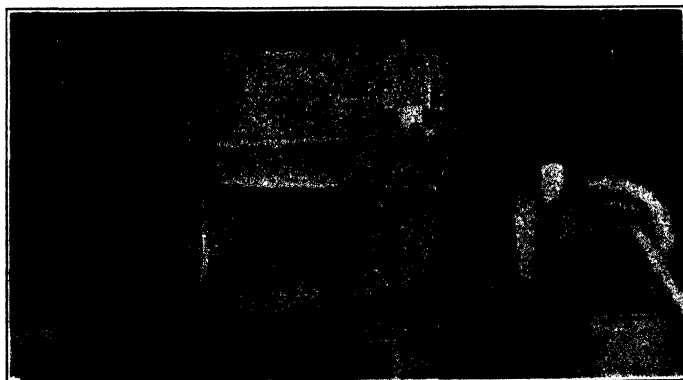


FIG. 2.—MUFFLE OPEN, CONES READY FOR FURNACES.

This brick was 6 by $4\frac{1}{4}$ by $1\frac{1}{8}$ in. The carborundum was bonded with a mixture of dextrine and molasses in water; this bond gave better results than either dextrine or molasses in water. The dextrine did not seem to have sufficient adhesion to hold the cones well; the molasses softened

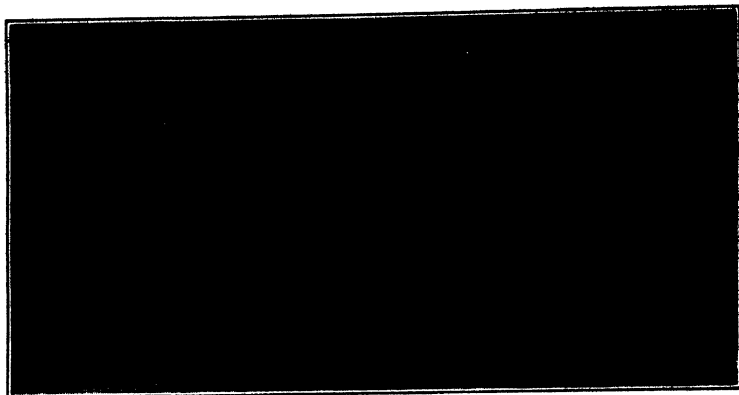


FIG. 3.—MUFFLE CLOSED AND PYROMETER INSERTED.

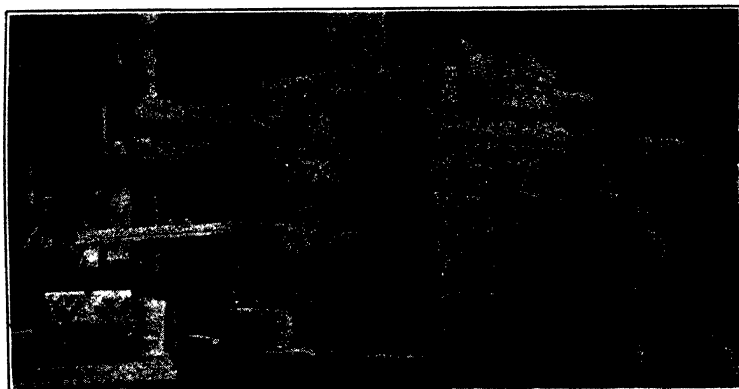


FIG. 4.—MUFFLE OPEN FOR INSPECTION.

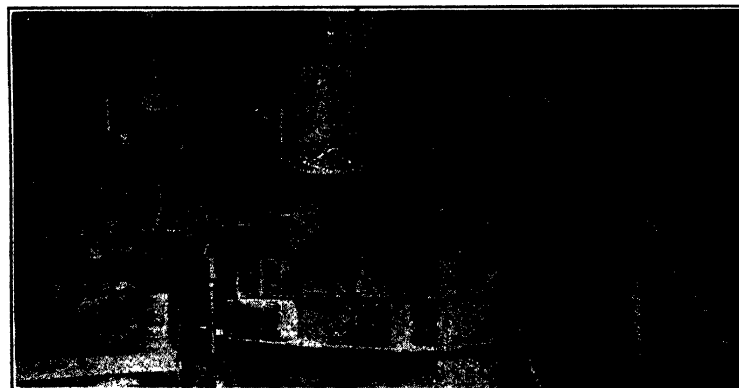


FIG. 5.—MUFFLE OPEN FOR USE OF OPTICAL PYROMETER.

to a very inconvenient extent when placing the mountings in the furnace. Each cone was placed on the carborundum while the latter was moist. Sufficient pressure was applied to make the cone penetrate the carborundum to a depth of about $\frac{1}{32}$ in. so that each cone was seated in a slight depression. No other material was used for mounting.

On each brick were placed fifteen cones in three rows of five each. After mounting, the assembly was set away to dry preferably for 48 hr. They can be dried in 2 or 3 hr. on the top of a hot furnace but the writer experienced less trouble with the crumbling of the carborundum and falling of cones when the assembly was dried slowly. After drying for

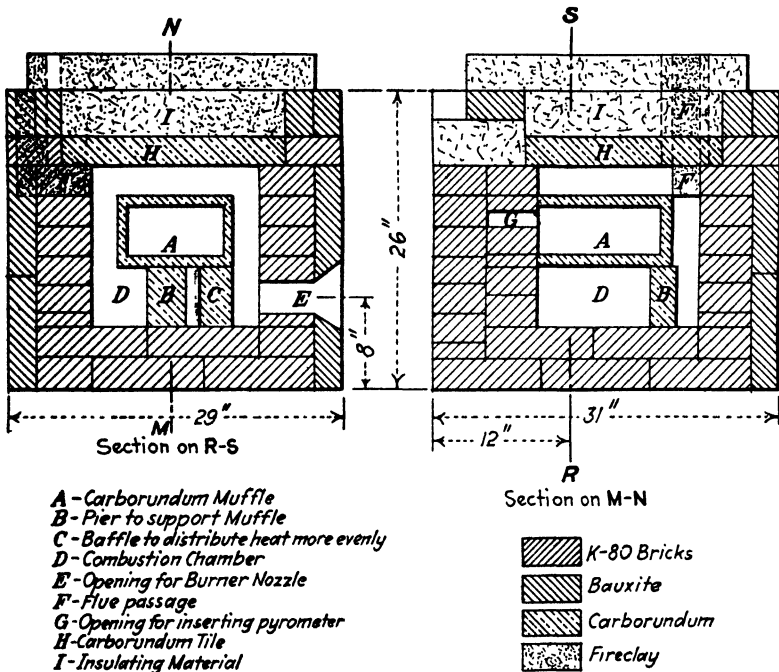


FIG. 6.—CONSTRUCTION OF FURNACE.

48 hr., the assembly was placed on the top of a furnace, where the temperature was 90 to 100° C., for 2 hr. The cones were then ready for the furnace.

Melting Tests

The furnace was first heated to a temperature in the muffle between 1300° C. and 1400° C.; this usually took about 3 hr. If the furnace had been out of use over 10 hr., about $4\frac{1}{2}$ to 5 hr. were required to heat up. If cones were placed in a cold furnace, the temperature of the air above the firebrick cone support would be much higher than the temperature of the brick, so that the point of the cone would be at one temperature and the base at another. This difference was found to be as much as 200° C.

Under this condition, it was impossible to get even an approximate determination of the temperature at which the cone fused. When the temperature in the muffle had reached 1300° to 1400° C., the gas was turned off and the muffle opened and allowed to cool as rapidly as possible to a temperature below the estimated softening point of the lowest melting cone in the sets that were to be run. Two firebricks, each with 15 cones, were put in the muffle; this placed the front row of cones about 4½ in. from the front of the muffle. The muffle was then closed and the furnace allowed to stand until the temperature of the firebrick and muffle were practically the same. In the preliminary heating of the furnace, the cooling of the muffle, and the equalizing of the temperature of the firebrick cone supports and the muffle, the aim was to have as great a reserve of heat as possible at a temperature just below the estimated softening point of the cones, so that when equilibrium was established the temperature would be near the melting point. Attempts were made to run the furnace on a reduced gas input and in that way keep temperatures uniform. This was not successful because the smallest gas input possible with this burner heated the muffle more rapidly than the brick and it was not possible to get a uniform temperature. If for any reason the muffle cooled to a lower temperature than was desired, it was found advisable to heat the furnace until the temperature in the muffle was as close to the formation temperature of the cones as possible. The gas was then shut off and all temperatures allowed to equalize before the final heating was started.

When all temperatures were practically uniform and as near the estimated softening temperature of the cones as possible, the gas was turned on and the furnace heated as rapidly as possible. Observations were made at 10° C. intervals until the first cone showed signs of softening or melting, after which the observations were practically continuous until the close of the run. The muffle was then opened, the brick removed, the gas turned off, and the furnace cooled preparatory to the next run.

Atmospheric Conditions

It is possible, in furnace work, to have a reducing, a neutral, or an oxidizing atmosphere. All three were tried. A reducing atmosphere was maintained by running the gas burner with an excess of gas and allowing some of the gas to escape around the openings at the front of the muffle; this kept the outside air from entering the muffle. In the muffle was placed a large quantity of gas carbon. These conditions produced a moderate reducing atmosphere. To obtain an oxidizing atmosphere, no special conditions were necessary. The neutral atmosphere was the more difficult to obtain. The burner was run with just as near a neutral flame as possible and a sufficient quantity of gas was allowed to escape

through the openings at the front of the muffle so that there was an out-flow of gas through all openings.

When the conditions in the muffle were reducing, there was a reaction between the zinc oxide and the carbon compounds in the gas and from the coke. The vaporized zinc escaped with the gas at the front of the muffle in sufficient quantities to make the fumes of zinc oxide distinctly visible. For this reason, the use of a reducing atmosphere was abandoned. An oxidizing condition was not wanted, for it would oxidize a part or all of the ferrous oxide to some higher oxide. In all the work, it was attempted to keep the atmosphere in the muffle as nearly neutral as possible. In this way the reduction of the zinc oxide and the oxidation of the ferrous oxide were prevented.

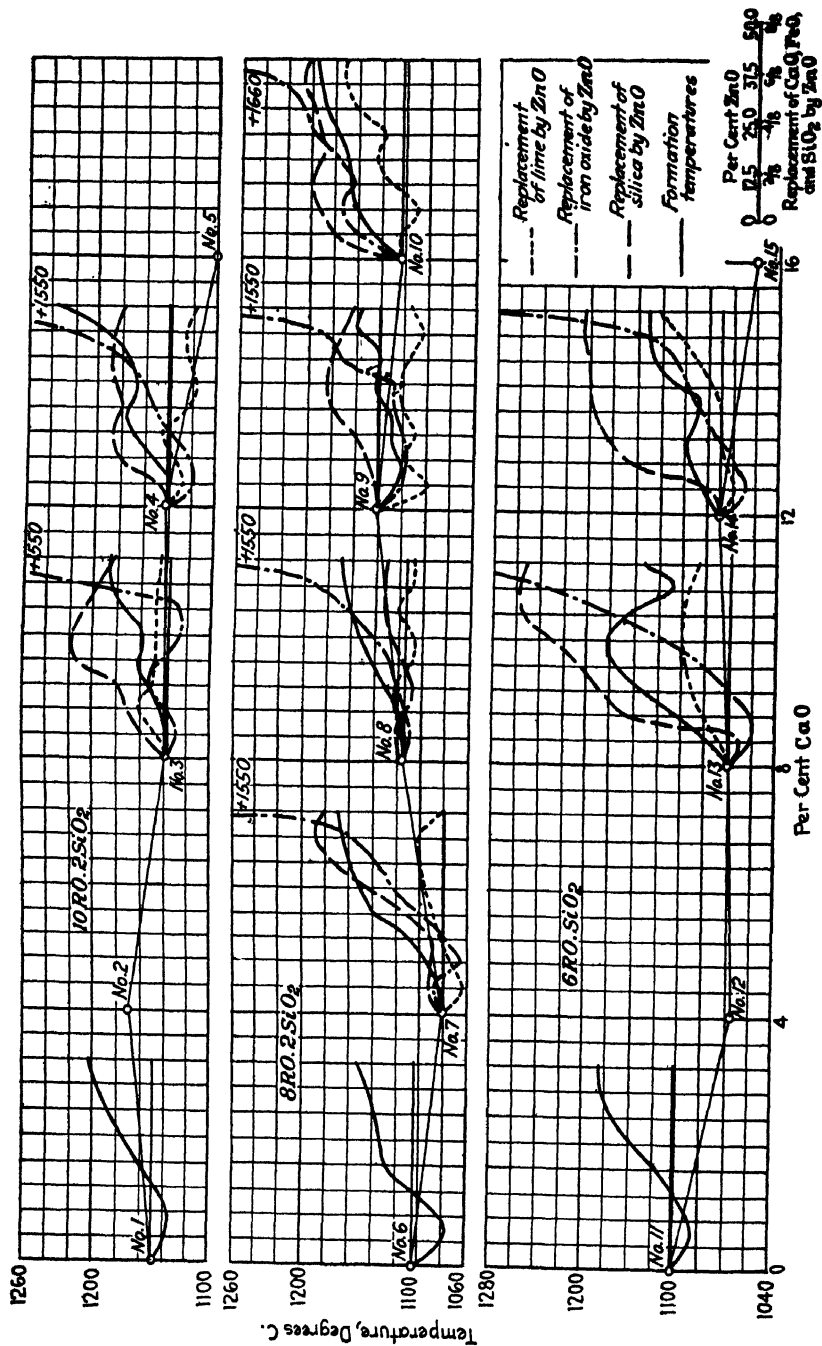
Temperature Measurements

All temperature measurements up to 1500° C. were made with a platinum and platinum-10 per cent. iridium thermocouple and a potentiometer. This thermocouple was standardized against the melting points of lead, antimony, and copper. The couple was protected by quartz tubing, which at the higher temperatures had a very short life. For temperatures above 1500° C., a Scimatco optical pyrometer was used. This instrument was standardized in the usual way with amyl acetate and then the two instruments were compared. The variation was about 20° C., the optical giving the higher temperature. During the course of the work, the two instruments were compared at the start and close of each day's work. The comparisons were made at temperatures of 1200° C. or higher and no appreciable variations from that found at the start of the work were observed.

Temperature Range during Melting and Viscosity

The preliminary idea was to obtain the temperature range from the point of incipient fusion, as shown by the rounding of the edges of the cone and its conversion into a liquid. This was not possible because of the great variation in the behavior of the cones. A few cones acted in the normal manner of seger cones: the edges and point softened, then the cone bent until the point touched the support, finally it liquefied. Most of the cones gave no indication as to their condition until they were liquid. A cone would be standing and show no signs of fusion, yet with a temperature change of 10° C. or less it would be completely liquefied. It did not bend at all but merely collapsed as if its support had been removed. A few cones seemed to shrink without any sign of fusion and then suddenly collapsed.

The plan of determining the viscosity was abandoned, for most of the slags, as soon as they become liquid, evolved gas very rapidly and zinc was



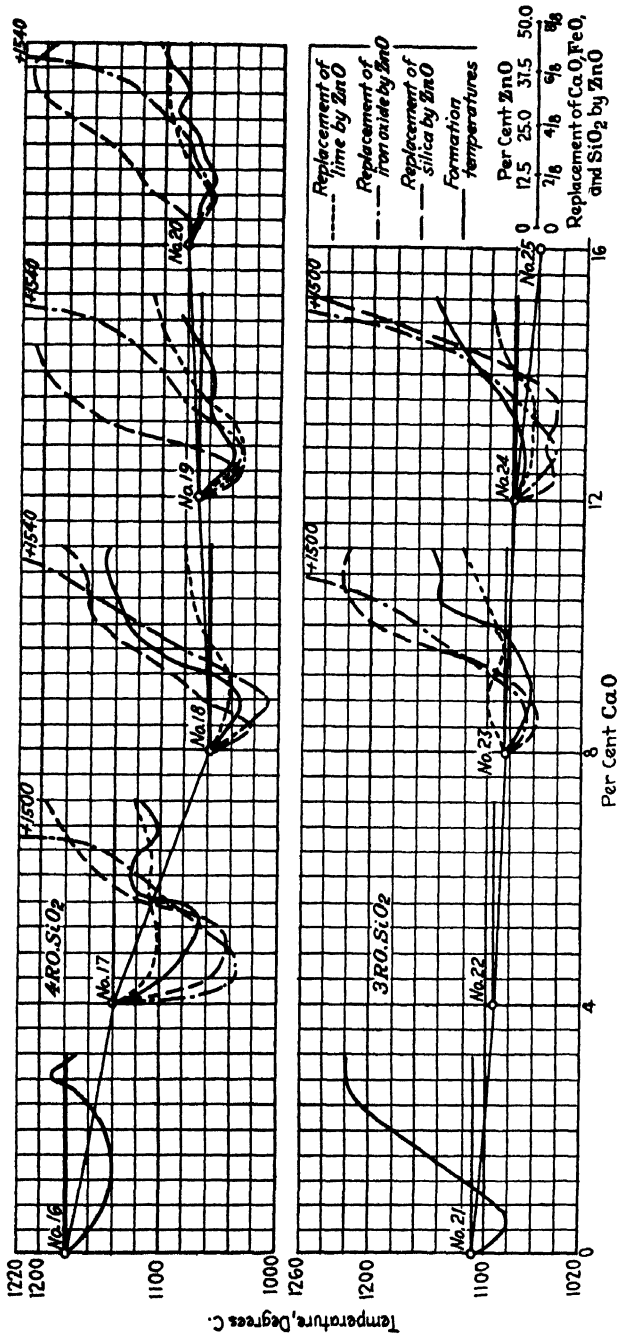


FIG. 7.—FORMATION TEMPERATURES.

given off copiously. The viscosity of the slag, after it had lost a portion of its zinc oxide, was of no interest. This was not true of the slags that did not contain zinc but their viscosity is fairly well known.

DISCUSSION

The formation temperatures are plotted in Fig. 7. The horizontal axis gives the calcium-oxide content of the basal slags; these basal slags are connected by a light solid line. At the point of each basal slag is a minor horizontal axis. This has two scales, one showing the percentage of zinc oxide in the basal slag after each addition of zinc oxide. Each division is equivalent to 6.66 per cent., the total being equivalent to 50 per cent. of zinc oxide in the basal slag. The second scale is for the replacement of lime (CaO), iron oxide (FeO), and silica (SiO_2) by zinc oxide and each division represents the replacement of one eighth of the total material present in the basal slag by an oxygen equivalent quantity of zinc oxide. The temperature scale is the same for all curves.

The iron silicates show a minimum, in all but one case, on the addition of 9 per cent. zinc. This gives an increase in the ratio SiO_2/ZnO varying from 1.57 to 3.56 as the silica or acidity of the slag increases. This increase is not regular. These slags are of little interest in non-ferrous metallurgy as they have a high specific gravity and therefore trouble would be experienced in separating the bullion and matte from the slag.

The addition of zinc to the basal slags containing lime shows a minimum in eight cases out of sixteen. The formation temperatures make very irregular curves. The general tendency is for the formation temperature of the slag to rise sharply with additions of more than 10 per cent. zinc. The irregularity of these curves is to be expected when one considers that two of the four elements present can act as either an acid or a base, depending on conditions which are practically unknown at the present time. Also the basic slags low in lime are good solvents and the possible solutions and combinations are great.

The replacement of lime (CaO) by zinc oxide gives rather irregular results. Some slags show a minimum, others show a maximum and then a minimum, others show two minimums, while others give an almost smooth curve rising as the temperature rises. At first glance, one is surprised at the smallness of the effects produced by replacing the lime by zinc oxide with that produced by replacing the other materials. In these slags the lime is low so that when all of the lime is replaced the slag seldom contains over 20 per cent. zinc oxide; while with the replacement of the silica and iron, and the addition of zinc oxide to the basal slag, it usually reaches a total of 50 per cent. or more.

The effect of substituting barium and magnesium for a part or all of the lime was not investigated. We know that zinc-barium slags, in

general, have lower formation temperatures than zinc-calcium slags. But barium increases the specific gravity of slags and most of these slags have a specific gravity very close to if not above the economic limit. The magnesium, if present in any considerable amount, raises the melting temperature so that its use is to be avoided if possible.

Attempts to classify the results so far have proved failures. If the minimums are considered, there is no apparent relation between the percentage of silica and the percentage of zinc oxide, other than that the ratio silica to zinc oxide becomes progressively less as the lime content increases; in a measure this ratio decreases as the acidity of the slag increases. All attempts to work out a constant that will even approximate the results obtained have so far failed.

Replacement of Iron Oxide by Zinc Oxide

Taking the thirteen curves that show a minimum, the ratio of silica to zinc oxide varies between 1.24 and 3.18. This ratio increases as the lime content of the slag increases and as the acidity increases; the increase is not regular. After the minimum point is reached, the formation temperature rises making a fairly smooth curve. The temperature at which the calcium silicate with a high percentage of zinc fuses was not determined. It is well above the temperature at which the firebrick became plastic.

These curves show that the iron requires close regulation. Most blast furnaces are driven at just about their limit so that any change in the composition of the charge which requires a great increase in the quantity of heat supplied per unit of charge usually slows down the furnace. This decrease in tonnage increases the cost of treatment per ton to such an extent that it is seldom permissible. If the change is too great, the charge must be changed or the furnace will freeze.

Replacement of Silica by Zinc Oxide

With the exception of two slags, No. 8 and No. 19, the ratio of silica to zinc oxide for the minimum is between 2.58 and 2.61. These curves also rise very rapidly once the minimum is passed, and indicate that the charge mixing for the furnace will have to be done very carefully if furnace troubles are to be avoided.

CONCLUSIONS

The difference between the formation temperature and the running temperature was small in most cases. Few slags were encountered that would cause any appreciable trouble in furnace operations due to a pasty stage.

The addition of zinc oxide to the basal slags, in excess of about 10 per cent., generally increased the formation temperature of the slags. This increase is not regular for a given slag and is not uniform between the various slags.

The effect of the replacement of the lime by zinc oxide is irregular and small. The formation temperatures, in general, are lowered on the addition of small quantities of zinc oxide and then increase as the percentage of zinc oxide increases.

The replacement of the silica by zinc oxide, in general, causes a lowering of the formation temperature and then an increase. This increase is greater with the more acid slags.

The replacement of the iron oxide by zinc oxide gives the more uniform results. In general, there is, first, a lowering followed by a rise in the formation temperature. This rise in most cases is rapid so that the ratio of iron to zinc in the charge will require careful regulation.

As a whole, this work shows that there are a large number of combinations that can be run on the modern furnace and produce a high-zinc slag, but that any furnace running on any of the slags high in zinc will require careful handling if serious troubles are to be avoided.

Slight changes in either the percentage of silica or iron oxide require great changes in the ratio of fuel to charge. If the charges are not proportioned carefully and mixed thoroughly, the furnace will be burdened with material that has a slag-formation temperature higher than that which the furnace can produce.

COMPOSITION OF SLAGS

Per Cent. SiO ₂	Per Cent. FeO	Per Cent. CaO	Per Cent. ZnO	Formation Temperature, Degrees C.
Slag No. 1—10RO.2SiO ₂				
14.30	85.70	0.0	0.0	1150
13.0	77.9	0.0	9.1	1136
11.9	71.4	0.0	16.7	1146
11.0	65.9	0.0	23.1	1160
10.2	61.2	0.0	28.6	1168
9.5	57.2	0.0	33.3	1180
8.9	53.6	0.0	37.5	1190
8.4	50.4	0.0	41.2	1190
7.9	47.6	0.0	44.5	1198
7.2	42.8	0.0	50.00	1206
Slag No. 2				
14.5	81.6	4.0	0.0	1170
Slag No. 3—10RO.SiO ₂				
14.62	77.38	8.00	0.00	1139
14.6	77.0	7.0	1.4	1150
14.5	76.7	5.9	2.9	1163
14.4	76.4	5.0	4.2	1153
14.4	76.0	3.9	5.7	1151
14.3	75.6	3.0	7.1	1152
14.2	75.3	2.0	8.5	1158
14.2	75.0	1.0	9.8	1148
14.1	74.7	0.0	11.2	1144
14.5	66.8	7.9	10.8	1133
14.3	56.5	7.8	21.4	1139
14.0	46.6	7.7	31.7	1145
13.9	36.7	7.6	41.8	1134
13.7	27.3	7.5	51.5	1130
13.6	18.0	7.4	61.0	1131
13.4	8.9	7.3	70.4	1220
13.2	0.0	7.3	79.5	1500
12.3	75.1	7.8	4.8	1160
10.4	72.9	7.5	9.2	1173
8.4	70.8	7.3	13.5	1180
6.5	68.9	7.1	17.5	1217
4.8	67.0	6.9	21.3	1220
3.1	65.2	6.8	24.9	1212
1.5	63.8	6.6	28.1	1200
0.0	62.1	6.4	31.5	1184
Slag No. 3—10RO.SiO ₂				
13.3	70.3	7.3	9.1	1142
12.2	64.4	6.7	16.7	1156
11.3	59.5	6.1	23.1	1164
10.4	55.3	5.8	28.5	1160
9.8	51.5	5.4	33.3	1166
9.2	48.3	5.0	37.5	1180
8.6	45.6	4.7	41.1	1190
8.2	43.0	4.4	44.4	1191
7.3	38.7	4.0	50.00	1189
Slag No. 4—10RO.SiO ₂				
14.8	73.2	12.0	0.0	1143
14.7	72.9	10.3	2.1	1130
14.6	72.3	8.9	4.2	1139
14.5	71.8	7.4	6.3	1148
14.5	71.3	5.8	8.4	1125
14.4	70.8	4.4	10.4	1120
14.2	70.5	2.9	12.4	1124
14.2	70.5	1.4	14.4	1128
14.1	70.0	0.0	16.3	1118
14.1	69.6	11.7	11.0	1120
14.5	62.8	11.5	21.5	1122
14.2	52.8	11.5	31.7	1143
13.8	43.2	11.3	41.5	1157
13.6	33.8	11.1	50.8	1163
13.4	24.9	10.9		

COMPOSITION OF SLAGS

Per Cent. SiO ₂	Per Cent. FeO	Per Cent. CaO	Per Cent. ZnO	Formation Temperature, Degrees C.
Slag No. 4—10RO.SiO ₂ (Continued)				
13.1	16.3	10.7	59.9	1182
12.9	8.0	10.5	68.6	1235
12.7	0.0	10.3	77.0	1500
12.6	71.1	11.6	4.8	1152
10.4	69.0	11.3	9.3	1186
8.5	66.8	11.0	13.7	1190
6.6	65.1	10.7	17.6	1180
4.8	63.4	10.4	21.4	1190
3.1	61.7	10.1	25.1	1193
1.5	60.2	9.8	28.5	1190
0.0	58.6	9.6	31.8	1180
Slag No. 4—10RO.2SiO ₂				
13.5	66.5	10.9	9.1	1148
12.2	61.1	10.0	16.7	1172
11.4	56.3	9.2	23.1	1180
10.6	52.3	8.6	28.5	1172
9.9	48.8	8.0	33.3	1170
9.2	45.8	7.5	37.5	1175
8.8	43.1	7.0	41.1	1190
8.2	40.7	6.7	44.4	1179
7.4	36.6	6.0	50.0	1240
Slag No. 5—10RO.2SiO ₂				
14.9	69.1	16.0	0.0	1100
Slag No. 6—8RO.2SiO ₂				
17.2	82.8	0.0	0.0	1105
15.6	75.3	0.0	9.1	1077
14.3	69.0	0.0	16.7	1105
13.2	63.7	0.0	23.1	1131
12.3	59.2	0.0	28.5	1132
11.5	55.2	0.0	33.3	1137
10.8	51.7	0.0	37.5	1142
10.1	48.7	0.0	41.2	1147
9.6	46.0	0.0	44.4	1152
8.6	41.4	0.0	50.0	1155
Slag No. 7—8RO.2SiO ₂				
17.4	78.6	4.0	0.0	1080
17.4	78.4	3.5	.7	1090
17.3	78.3	3.0	1.4	1067
17.2	78.1	2.5	2.2	1083
17.2	77.9	2.0	2.9	1090
17.2	77.7	1.5	3.6	1095
17.2	77.5	1.0	4.3	1100
17.1	77.4	0.5	5.0	1102
17.1	77.2	0.0	5.7	1082
17.2	67.9	4.0	10.9	1065
17.0	57.5	3.9	21.6	1075
16.8	47.3	3.8	32.1	1080
16.5	37.4	3.8	42.3	1120
16.4	27.6	3.8	52.2	1125
16.2	18.3	3.7	61.8	1163
16.0	9.0	3.6	71.4	1160
15.9	0.0	3.6	80.5	1160
14.7	75.8	3.9	5.6	1400
12.2	73.2	3.7	10.9	1112
9.8	70.8	3.6	15.8	1110
7.6	68.5	3.5	20.4	1112
5.5	66.5	3.4	24.6	1136
3.6	64.4	3.3	28.7	1165
1.7	62.6	3.2	32.5	1197
0.0	60.7	3.1	36.2	1210
				1200

COMPOSITION OF SLAGS

Per Cent. SiO ₂	Per Cent. FeO	Per Cent. CaO	Per Cent. ZnO	Formation Temperature, Degrees C.
Slag No. 7				
15.8	71.5	3.6	9.1	1090
14.5	65.5	3.3	16.7	1105
13.4	60.4	3.1	23.1	1139
12.4	56.2	2.8	28.6	1147
11.6	52.4	2.7	33.8	1152
10.9	49.1	2.5	37.5	1157
10.2	46.2	2.4	41.2	1168
9.7	43.7	2.2	44.4	1168
8.7	39.3	2.0	50.0	1171
Slag No. 8—8RO.2SiO ₂				
17.6	75.4	8.0	0.0	1115
17.6	74.0	7.0	1.4	1115
17.5	73.7	5.9	2.9	1123
17.4	73.5	4.9	4.2	1122
17.3	73.1	3.9	5.1	1110
17.2	72.8	2.9	7.1	1110
17.2	72.4	1.9	8.5	1122
17.1	72.2	0.9	9.8	1112
17.0	71.8	0.0	11.2	1112
17.4	64.4	7.8	10.3	1112
17.2	54.4	7.8	20.6	1118
17.0	44.8	7.7	30.5	1123
16.8	35.6	7.6	40.0	1128
16.6	26.3	7.6	49.5	1134
16.4	17.4	7.5	58.7	1150
16.3	8.6	7.4	67.7	1174
16.1	0.0	7.3	75.6	1500
14.9	71.7	7.7	5.7	1122
12.3	69.3	7.4	11.0	1115
10.0	66.9	7.2	15.9	1108
7.7	64.8	7.0	20.5	1118
5.6	63.8	6.7	24.9	1128
3.6	60.9	6.5	29.0	1134
1.8	59.1	6.3	32.8	1133
0.0	57.4	6.2	36.4	1133
Slag No. 8—8RO.2SiO ₂				
16.0	67.6	7.3	9.1	1115
14.6	62.0	6.7	16.7	1136
13.5	57.3	6.1	23.1	1145
12.6	53.2	5.7	28.5	1152
11.7	49.7	5.3	33.3	1155
11.0	46.5	5.0	37.5	1152
10.3	43.8	4.7	41.2	1171
9.8	41.4	4.4	44.4	1171
8.8	37.2	4.0	50.0	1171
Slag No. 9—8RO.2SiO ₂				
17.8	70.2	12.0	00.0	1143
17.6	69.9	10.4	2.1	1100
17.5	69.3	8.9	4.3	1119
17.42	68.80	7.4	6.4	1109
17.3	68.4	5.8	8.5	1121
17.2	67.9	4.4	10.5	1123
17.1	67.5	2.9	12.5	1117
17.0	67.1	1.4	14.5	1105
16.9	66.6	0.0	16.5	1115
17.6	60.7	11.9	9.8	1121
17.4	51.5	11.8	19.3	1118
17.2	42.5	11.6	28.7	1136
17.0	33.7	11.5	37.8	1131
16.8	25.0	11.4	46.8	1131
16.7	16.5	11.3	55.5	1176
16.5	8.2	11.1	64.2	1190
16.4	0.0	11.0	72.6	1500
15.0	67.6	11.6	5.8	1145
12.4	65.3	11.2	11.1	1155
10.0	63.1	10.8	16.1	1160
7.7	61.1	10.5	20.7	1184
5.6	59.2	10.1	25.1	1187
3.6	57.4	9.8	29.2	1182
1.8	55.6	9.5	33.1	1187
0.0	54.1	9.2	36.7	1171

22 EFFECT OF ZINC OXIDE ON FORMATION OF FERROUS SLAGS

COMPOSITION OF SLAGS

Per Cent. SiO ₂	Per Cent. FeO	Per Cent. CaO	Per Cent. ZnO	Formation Temperature, Degrees C.
Slag No. 9—8RO.2SiO ₂				
16.2	63.8	10.9	9.1	1120
14.8	58.5	10.0	16.7	1131
13.7	54.0	9.2	23.1	1128
12.7	50.2	8.5	28.5	1145
11.8	46.8	8.0	33.3	1142
11.1	43.8	7.5	37.5	1142
10.60	41.3	7.0	41.1	1145
9.90	39.0	6.5	44.4	1161
8.9	35.1	6.0	50.0	1155
Slag No. 10—8RO.2SiO ₂				
18.0	66.0	16.0	0.0	1123
17.8	65.4	13.9	2.9	1123
17.7	64.8	11.8	5.7	1110
17.5	64.3	9.7	8.5	1137
17.4	63.6	7.8	11.2	1145
17.2	63.2	5.8	13.8	1137
17.1	62.6	3.8	16.5	1163
17.0	62.1	1.9	19.0	1173
16.8	61.6	0.0	21.6	1168
17.8	57.2	15.8	9.2	1163
17.6	48.5	15.7	18.2	1175
17.5	40.0	15.5	27.0	1168
17.3	31.7	15.4	35.6	1176
17.1	23.5	15.2	44.2	1200
17.0	15.5	15.1	52.4	1165
16.8	7.7	14.9	60.6	1222
16.6	0.0	14.8	68.6	1500
15.2	63.6	15.4	5.8	1185
12.5	61.4	14.9	11.2	1190
10.1	59.3	14.3	16.3	1200
7.8	57.3	13.9	21.0	1190
5.7	55.4	13.5	25.4	1195
3.7	53.8	13.0	29.5	1195
1.8	51.9	12.6	33.7	1208
0.0	50.6	12.3	37.1	1202
Slag No. 10—8RO.2SiO ₂				
16.4	60.0	14.5	9.1	1160
15.0	55.0	13.3	16.7	1170
13.8	50.8	12.3	23.1	1170
12.9	47.1	11.4	28.5	1170
12.0	44.0	10.7	33.3	1181
11.8	41.2	10.0	37.5	1189
10.6	38.8	9.4	41.2	1189
10.0	36.7	8.9	44.4	1189
9.0	33.0	8.0	50.0	1195
Slag No. 11—6RO.2SiO ₂				
21.70	78.30	0.00	0.00	1122
19.7	71.2	0.0	9.1	1106
18.1	65.2	0.0	16.7	1120
16.7	60.2	0.0	23.1	1134
15.5	55.9	0.0	28.6	1152
14.5	52.2	0.0	33.3	1156
13.6	48.9	0.0	37.5	1176
12.9	46.0	0.0	41.1	1180
12.1	43.5	0.0	44.4	1184
10.9	39.1	0.0	50.0	1186
Slag No. 12				
22.0	74.0	4.0	0.0	1174

COMPOSITION OF SLAGS

Per Cent. SiO ₂	Per Cent. FeO	Per Cent. CaO	Per Cent. ZnO	Formation Temperature, Degrees C.
Slag No. 13—6RO.2SiO ₂				
22.20	69.80	8.00	0.0	1080
22.1	69.5	7.0	1.4	1085
22.0	69.2	5.9	2.9	1105
22.0	68.9	4.9	4.2	1110
21.8	68.6	3.9	5.7	1115
21.7	68.3	2.9	7.1	1120
21.6	68.0	1.9	8.5	1120
21.6	67.7	0.9	9.8	1115
21.5	67.4	0.0	11.1	1107
22.0	60.4	7.9	9.7	1065
21.7	51.2	7.8	19.3	1060
21.5	42.3	7.7	28.5	1080
21.3	33.4	7.7	37.6	1105
21.0	24.8	7.6	46.6	1137
20.8	16.4	7.5	55.3	1184
20.6	8.2	7.4	63.8	1240
20.4	0.0	7.4	72.2	1428
18.6	67.0	7.7	6.7	1075
15.2	63.8	7.3	13.7	1167
12.1	61.2	7.1	19.6	1190
9.4	58.7	6.7	25.2	1205
6.6	56.6	6.5	30.3	1230
4.3	54.4	6.3	35.0	1255
2.1	52.5	6.0	39.4	1255
0.0	50.8	5.8	43.4	1250
Slag No. 13—6RO.2SiO ₂				
20.2	63.4	7.3	9.1	1115
18.5	58.2	6.6	16.7	1152
17.1	53.6	6.2	23.1	1170
15.9	49.8	5.7	28.6	1182
14.8	46.6	5.3	33.3	1180
13.9	43.6	5.0	37.5	1159
13.1	41.1	4.7	41.1	1140
12.4	38.8	4.4	44.4	1130
11.1	34.9	4.0	50.0	1153
Slag No. 14—6RO.2SiO ₂				
22.49	65.51	12.00	0.000	1092
22.4	65.1	10.4	2.1	1080
22.2	64.7	8.9	4.2	1087
22.0	64.4	7.3	6.3	1087
21.5	63.9	5.8	8.4	1090
21.8	63.4	4.3	10.5	1098
21.7	63.0	2.9	12.4	1110
21.5	62.7	1.4	14.4	1125
21.4	62.3	0.0	16.3	1143
22.3	56.7	11.9	9.1	1070
22.1	48.1	11.8	18.0	1080
21.8	39.7	11.7	26.8	1094
21.6	31.5	11.5	35.4	1107
21.4	23.4	11.4	43.8	1120
21.2	15.5	11.3	52.0	1126
21.0	7.7	11.2	60.1	1157
20.8	0.0	11.1	68.1	1500
18.8	62.5	11.5	7.2	1100
15.3	59.9	11.0	13.8	1168
12.3	57.4	10.5	19.8	1185
19.5	55.0	10.1	25.4	1195
6.8	53.0	9.7	30.5	1200
4.4	51.0	9.3	35.3	1200
2.1	49.2	9.0	39.7	1208
0.0	47.5	8.7	43.8	1205

24 EFFECT OF ZINC OXIDE ON FORMATION OF FERROUS SLAGS

COMPOSITION OF SLAGS

Per Cent. SiO ₂	Per Cent. FeO	Per Cent. CaO	Per Cent. ZnO	Formation Temperature, Degrees C.
Slag No. 14—6RO.2SiO ₂				
20.5	59.5	10.9	9.1	1112
18.7	53.6	10.0	16.7	1120
17.3	50.4	9.2	23.1	1112
16.1	46.7	8.6	28.6	1110
15.0	43.7	8.0	33.3	1136
14.1	40.9	7.5	37.5	1147
13.2	38.6	7.1	41.1	1147
12.5	36.4	6.7	44.4	1150
11.3	32.7	6.0	50.0	1153
Slag No. 15				
22.7	61.3	16.0	0.0	1060
Slag No. 16—4RO.2SiO ₂				
29.2	70.8		0.0	1179
26.6	64.3		9.1	1151
24.3	59.0		16.7	1144
22.5	54.4		23.1	1142
20.8	50.6		28.6	1147
19.5	47.2		33.3	1149
18.2	44.3		37.5	1160
17.2	41.6		41.2	1170
16.2	39.4		44.4	1192
14.6	35.4		50.0	1168
Slag No. 17				
29.7	66.3	4.0	0.0	1140
29.7	66.3	3.3	0.7	1110
29.7	66.2	2.8	1.3	1105
29.6	66.0	2.4	2.0	1100
29.6	66.0	1.8	2.6	1110
29.5	65.7	1.4	3.4	1108
29.4	65.6	1.0	4.0	1108
29.4	65.6	0.5	4.5	1116
29.2	64.6	0.0	5.4	1122
29.5	57.5	3.9	9.1	1035
29.3	48.7	3.9	18.1	1035
28.9	40.2	3.9	27.0	1075
28.7	31.9	3.9	35.5	1085
28.5	23.7	3.8	44.0	1108
28.1	15.7	3.8	52.4	1147
27.9	7.7	3.7	60.7	1500
27.7	0.0	3.7	68.6	1500
24.4	62.4	3.8	9.4	1060
19.9	58.9	3.5	17.7	1045
15.6	55.8	3.4	25.2	1052
12.0	52.8	3.2	32.0	1119
8.6	50.3	3.1	38.0	1147
5.3	48.4	2.9	43.4	1162
2.6	46.1	2.8	48.5	1184
0.0	44.2	2.7	53.1	1199
Slag No. 17				
27.1	60.2	3.6	9.1	1085
25.9	57.6	3.5	13.0	1080
24.8	55.2	3.3	16.7	1080
23.8	53.0	3.2	20.0	1070
22.9	51.0	3.1	23.0	1059
22.1	49.9	3.0	26.0	1120
21.3	47.4	2.8	28.5	1120
19.7	44.3	2.7	33.3	1126
18.5	41.5	2.5	37.5	1120
16.6	36.8	2.2	44.4	1100
14.9	32.1	2.0	50.0	1118

COMPOSITION OF SLAGS

Per Cent. SiO ₂	Per Cent. FeO	Per Cent. CaO	Per Cent. ZnO	Formation Temperature, Degrees C.
Slag No. 18—4RO.2SiO ₂				
30.1	61.9	8.0	0.0	1060
30.0	61.7	7.0	1.3	1050
30.0	61.4	6.0	2.6	1050
30.0	61.0	4.9	4.1	1040
29.9	60.9	3.9	5.3	1060
29.7	60.5	2.8	7.0	1070
29.3	60.3	1.9	8.4	1070
29.2	60.0	1.0	9.8	1080
29.2	59.6	0.0	11.2	1080
29.7	53.7	7.9	8.7	1040
29.5	45.5	7.9	17.1	1010
29.2	37.5	7.8	25.5	1050
28.9	29.9	7.7	33.5	1080
28.6	20.2	7.6	41.6	1115
28.4	14.6	7.5	49.5	1163
28.1	7.3	7.4	57.2	1184
27.9	0.0	7.4	64.7	1540
24.8	58.2	7.5	9.5	1030
20.0	54.7	7.1	18.2	1070
15.8	51.8	6.7	25.7	1090
12.0	49.3	6.4	32.3	1131
8.5	46.9	6.1	38.5	1163
5.5	44.7	5.8	44.0	1163
2.6	42.8	5.5	49.1	1163
0.0	40.9	5.3	53.8	1184
Slag No. 18—4RO.2SiO ₂				
27.4	56.2	7.3	9.1	1040
26.2	53.8	7.0	13.0	1035
25.1	51.5	6.7	16.7	1045
23.1	47.5	6.3	23.1	1100
21.5	44.2	5.7	28.6	1131
20.1	41.3	5.3	33.3	1131
18.0	38.7	5.0	37.5	1142
16.6	34.3	4.4	44.5	1152
15.1	30.9	4.0	50.0	1147
Slag No. 19—4RO.2SiO ₂				
30.4	57.6	12.0	0.0	1070
30.2	57.2	10.4	2.2	1045
30.0	56.9	8.9	4.2	1035
29.9	56.6	7.3	6.2	1040
29.6	56.1	5.8	8.5	1070
29.4	55.3	4.3	10.5	1080
29.3	55.4	2.9	12.4	1095
29.1	55.1	1.4	14.4	1100
28.9	54.7	0.0	16.4	1110
30.1	49.9	11.9	8.1	1035
29.9	42.4	11.8	15.9	1035
29.6	35.0	11.7	23.7	1060
29.2	27.7	11.6	31.5	1090
29.0	20.7	11.4	38.9	1105
28.8	13.6	11.4	46.2	1131
28.5	6.7	11.3	53.5	1163
28.3	0.0	11.2	60.5	1540
25.0	54.1	11.3	9.6	1035
20.3	51.0	10.6	18.1	1080
15.9	48.4	10.0	25.7	1160
12.0	44.9	9.5	32.6	1174
8.6	43.7	9.1	38.6	1205
5.5	41.5	8.7	44.6	1210
2.6	39.7	8.3	49.4	1205
0.0	38.0	8.0	54.0	1184

COMPOSITION OF SLAGS

Per Cent. SiO ₂	Per Cent. FeO	Per Cent. CaO	Per Cent. ZnO	Formation Temperature, Degrees C.
Slag No. 19—4RO.2SiO ₂				
29.0	54.9	11.4	4.7	1040
27.8	52.2	10.9	9.1	1055
26.5	50.0	10.5	13.0	1062
25.3	48.0	10.0	16.7	1055
24.3	46.1	9.6	20.0	1067
23.4	44.3	9.2	23.1	1055
21.6	41.3	8.6	28.5	1081
19.0	36.0	7.5	37.5	1085
Slag No. 20—3RO.2SiO ₂				
30.8	53.2	16.0	0.0	1082
30.5	52.7	13.8	3.0	1070
30.2	52.3	11.8	5.7	1060
30.0	51.8	9.7	8.5	1080
29.7	51.4	7.7	11.2	1087
29.5	51.0	5.7	13.8	1095
29.3	50.4	3.8	16.5	1097
29.0	50.0	2.0	19.0	1097
28.8	49.6	0.0	21.6	1107
30.6	46.2	15.8	7.4	1075
30.1	38.6	15.6	14.7	1060
30.0	32.5	15.5	22.0	1075
29.8	25.8	15.4	29.0	1080
29.6	19.2	15.4	35.8	1100
29.2	12.8	15.2	42.8	1120
29.0	6.3	15.1	49.6	1174
28.8	0.0	15.0	56.2	1550
25.3	49.0	15.0	9.8	1080
20.4	47.1	14.2	18.8	1136
16.0	44.6	13.4	26.0	1147
12.1	42.3	12.7	32.9	1163
8.7	40.2	12.1	39.0	1180
5.5	38.3	11.6	44.6	1210
2.7	36.6	11.0	49.7	1215
0.0	35.2	10.6	54.2	1195
Slag No. 20—3RO.2SiO ₂				
28.0	48.4	14.5	9.1	1075
26.8	46.3	13.9	13.0	1060
25.7	44.3	13.3	16.7	1060
23.7	40.9	12.3	23.1	1070
22.0	38.0	11.5	28.5	1075
20.5	35.5	10.7	33.3	1095
19.2	33.3	10.0	37.5	1080
18.1	31.3	9.4	41.2	1085
17.2	29.5	8.9	44.4	1100
15.4	26.6	8.0	50.0	1100
Slag No. 21—3RO.2SiO ₂				
35.70	64.30	0.00	0.00	1105
32.5	58.4	0.00	9.1	1080
29.7	53.6	0.00	16.7	1120
27.4	49.5	0.00	23.1	1140
25.4	46.0	0.00	28.6	1163
23.8	42.9	0.00	33.3	1193
22.3	40.2	0.00	37.5	1215
21.0	37.8	0.00	41.2	1215
19.8	35.8	0.00	44.4	1215
17.8	32.2	0.00	50.0	1215
Slag Number 22				
36.0	60.0	4.0	0.0	1095

COMPOSITION OF SLAGS

Per Cent. SiO ₂	Per Cent. FeO	Per Cent. CaO	Per Cent. ZnO	Formation Temperature, Degrees C.
Slag No. 23—3RO.2SiO ₂				
36.40	55.60	8.00	0.00	1085
36.3	55.4	6.9	1.4	1095
36.1	55.2	5.9	2.8	1100
36.0	54.9	5.0	4.1	1095
35.7	54.6	4.0	5.7	1085
35.6	54.5	2.9	7.0	1090
35.5	54.2	1.9	8.4	1105
35.3	54.0	1.0	9.7	1115
35.2	53.6	0.0	11.2	1125
36.1	48.2	7.9	7.8	1065
35.8	40.8	7.9	15.5	1067
35.4	33.9	7.7	23.0	1095
35.0	26.9	7.7	30.4	1139
34.8	19.9	7.6	37.7	1160
34.6	13.2	7.5	44.7	1195
34.1	6.6	7.5	58.1	1500
33.9	0.0	7.4	58.7	1500
29.7	51.6	7.4	11.3	1057
23.7	48.2	6.9	21.2	1063
18.5	45.2	6.5	29.8	1085
13.9	42.5	6.1	37.5	1139
9.9	40.2	5.8	44.1	1200
6.1	38.2	5.5	50.2	1221
3.0	36.2	5.2	55.6	1230
0.0	34.5	5.0	60.5	1221
Slag No. 23—3RO.2SiO ₂				
33.1	56.5	7.3	9.1	1063
30.3	46.3	6.7	16.7	1063
28.0	42.7	6.2	23.1	1075
26.0	39.8	5.7	28.5	1085
24.3	37.1	5.3	33.3	1120
22.7	34.8	5.0	37.5	1145
21.4	33.7	4.7	41.2	1140
20.2	30.9	4.5	44.4	1141
18.2	27.8	4.0	50.0	1152
Slag No. 24—3RO.2SiO ₂				
36.8	51.2	12.0	0.0	1080
36.6	50.8	10.4	2.1	1070
36.3	50.5	8.9	4.3	1067
36.1	50.2	7.4	6.3	1065
35.9	49.9	5.8	8.4	1065
35.6	49.6	4.4	10.4	1078
35.4	49.3	2.9	12.4	1095
35.2	49.0	1.4	14.4	1100
35.0	48.7	0.0	16.3	1100
36.5	44.5	11.9	7.1	1055
36.2	37.8	11.8	14.2	1045
35.9	31.3	11.7	21.1	1060
35.7	24.8	11.6	27.9	1085
35.4	18.5	11.5	34.6	1110
35.1	12.3	11.4	41.2	1144
34.8	6.1	11.4	47.7	1220
34.6	0.0	11.3	54.1	1500
29.9	47.5	11.1	11.5	1045
23.9	44.3	10.4	21.4	1055
18.7	41.5	9.7	30.1	1045
14.0	39.1	9.2	37.7	1043
10.0	36.9	8.6	44.5	1080
6.3	34.9	8.2	50.6	1123
3.0	33.1	7.7	56.2	1195
0.0	31.6	7.4	61.0	1247
Slag No. 24—3RO.2SiO ₂				
33.5	46.5	10.0	9.1	1070
30.7	42.6	10.0	16.7	1075
28.3	39.4	9.2	23.1	1090
26.3	36.6	8.6	28.5	1104
24.6	34.1	8.0	33.3	1118
23.0	32.0	7.5	37.5	1128
21.6	30.1	7.1	41.2	1138
20.4	28.5	6.7	44.4	1138
18.4	25.6	6.0	50.0	1149

Slag No. 25

37.3

46.7

0.0

1053

DISCUSSION

G. E. DALBEY, East Berlin, Conn.—I had occasion to run a small circular blast furnace on brass ashes containing considerable metallic zinc. Much of this zinc was volatilized and the balance of it went in the slag. The slag would run about 41 per cent. FeO. The zinc oxide ran from 24 to 31 per cent., roughly, and the lime around 11 to 15 per cent.

I noticed that as long as we kept the furnace crowded and working fast we had no great difficulty, but if we hung up for a short time we could not get going again. Apparently the slag did not have a sharp freezing point. It ran smoothly for a time, then suddenly you would see coming out of a tap hole something like a mush of crystals floating in the liquid portion of the slag. What those crystals were, I do not know. I attribute this mush to a compound of zinc. The slag reminded me of a wiping solder, 40 per cent. Sn, 60 per cent. Pb, solidifying.

H. D. HIBBARD, Plainfield, N. J.—Some of these slags here are marked as having no silica. I am curious to know how a product of the earth can be without silica. In a slag like this does the iron act as an acid?

H. T. MANN.—I cannot say exactly. You might form a zincate or possibly a ferrite, but which it was I do not know.

C. R. HAYWARD, Cambridge, Mass.—I believe the figures on Fe and FeO that were questioned in the table have been confirmed. Perhaps that should be made a part of the record.

E. P. MATHEWSON, New York, N. Y.—I have only had occasion to note the very high zinc slags of the Burma Corporation. These are referred to in No. 7 and No. 8. They were very hot and ran nicely through the furnace. There was seldom any trouble with sudden freeze-up.

Years ago in Colorado we had experience with zincky slags, using a variety of ores. We had great trouble unless the iron was quite high in the slag. We ran successfully slags containing up to 12 per cent. Zn, even with considerable magnesia in the ores.

The lead in the Burma slags was a little high, but the zinc was very high, often as high as 26 to 28 per cent. I think they could have made the slags cleaner in lead if they had left sufficient sulfur to form a matte.

The secret of success in running high-zinc slags is to have no sulfur in the charge. If sulfide of zinc is present you will have a pasty slag. In fact, I remember that years ago in Colorado we would sometimes get crystals of sphalerite in the slags. Zinc sulfide would go through unaltered.

C. S. WITHERELL, New York, N. Y. (written discussion).—I wish to put before you some theoretical matter pertaining to impurities in general and zinc in particular, found in the lead and copper blast furnace slags.

In the past metallurgists have been in the habit of classifying all slag ingredients, other than silica, iron and lime, as equivalents of these three fundamental constituents. This principle may logically be roughly applied to such substances as magnesia for lime or manganese for iron; but in many, probably most, cases the substance under consideration cannot logically be considered a substitute for silica, iron or lime. Into this latter category I would place zinc and alumina.

I maintain that it is a more rational view to consider the extra-fundamental ingredients of the slag to be in the form of compounds dissolved by a primary slag made up of the fundamental ingredients, silica, iron and lime. This can be compared to the dissolving of scorified impurities in borax as commonly practiced in fire assaying. Based upon this line of reasoning one should first determine in what combination the extra-fundamental ingredient appears and then select a proper primary or solvent-slag for carrying it.

Several years ago it was thought that ferruginous slags were the best for carrying zinc; recent practice has shown that other slags also high in zinc can be used to advantage. Nevertheless, slags high in iron are good solvents of zinc; which leads me to believe that in such slags the zinc is combined with iron.

There are two zinc-iron compounds that may be considered, namely zinc-ferrate (or ferrite) $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$ and zincate of iron $\text{FeO} \cdot \text{ZnO}$. Since the iron in slags is practically always found in the ferrous state, the zincate of iron appears to be the more probable compound. Upon this assumption I present the following calculations:

Assume that the slag is fairly free of other ingredients and therefore the ZnO , SiO_2 , FeO and CaO total, say 90 per cent.

For the compound $\text{FeO} \cdot \text{ZnO}$ the following ratios obtain: wt. Zn to wt. ZnO equals 1:1.245, wt. ZnO to wt. FeO equals 1:0.883, wt. ZnO to wt. $\text{FeO} \cdot \text{ZnO}$ equals 1:1.883. Hence in the slag produced the amount of solvent-slag equals 90 per cent. minus $1.883 \times$ per cent. ZnO . Let us select for solvent-slag the composition 38 per cent. SiO_2 , 42 per cent. FeO , 20 per cent. CaO , and take for example a furnace slag containing 20 per cent. ZnO . Then the following can be calculated as shown:

Per cent. zincate, $20 \times 1.883 =$	37.66
Per cent. solvent-slag $90 - 37.66 =$	52.34
Per cent. FeO in solvent, $52.34 \times 0.42 =$	21.98
Per cent. FeO in zincate, $20 \times 0.883 =$	17.66
<hr/>	
Total per cent. FeO	39.64
Per cent. SiO_2 , 52.34×0.38	19.89
Per cent. CaO , 52.34×0.20	10.47
Per cent. ZnO	20.00
<hr/>	
	90.00

By using the foregoing assumptions and method of calculation the following table was compiled:

ZnO, Per Cent.	SiO ₂ , Per Cent.	FeO, Per Cent.	CaO, Per Cent.
0	34.20	37.80	18.00
5	30.62	38.26	16.12
10	27.05	38.72	14.23
15	23.47	39.18	12.35
20	19.89	39.64	10.47
25	16.31	40.10	8.59
30	12.73	40.57	6.70
35	9.16	41.02	4.82
40	5.58	41.48	2.94

It will be noted that in the iron zincate hypothesis when the iron assumed to be combined with the zinc is deducted the remaining slag need not be highly ferruginous.

I do not claim that a compound of zinc and iron is the only zinc compound that can form in a slag; recent practice indicates strongly to the contrary. Whatever the compound formed if it of itself does not constitute a workable slag, it must be dissolved in a solvent-slag to run it out of the furnace; on this basis should the slag composition be determined.

C. R. HAYWARD, Cambridge, Mass. (written discussion).—The discussion presented by Mr. Witherell is of considerable interest and his reasoning is entirely logical. The same theory was suggested several years ago by J. E. Johnson, Jr., in connection with iron blast-furnace slags.¹ He pointed out that several slags with widely varying alumina content had the same ratio of lime to silica which tended to show that the alumina was dissolved in the calcium silicate.

A. L. WALKER, New York, N. Y.—In almost all the slags I have noticed having a high-zinc content, the lead content was also high. Was the effect of zinc on the lead content in the slag considered in this paper?

C. R. HAYWARD.—This paper was presented wholly on a theoretical basis, taking chemically prepared materials. No attempt was made to add lead to it. It was felt that the scope of the paper should be kept wholly within the theoretical range, leaving the matter of lead content, etc., to future work.

A. L. WALKER.—I did not mean to state that a 3 per cent. slag was not the best slag that could be produced; as has been said, a metallurgist must also be a financier. My experience in the Southwest 40 years ago where we made a vast amount of slag containing 2 to 3 per cent. of copper, illustrates the point. It was the most profitable slag we could produce.

¹ Trans. (1912), XLIV, 123.

Recovery of Copper by Leaching, Ohio Copper Co. of Utah

BY ARVID E. ANDERSON AND FRANK K. CAMERON, BINGHAM, UTAH

(Salt Lake City Meeting, September, 1925)

THE weathering of copper-bearing ores with the formation of a water-soluble salt and the recovery of the metal by leaching and evaporation or precipitation, are processes long known, which have at various times been utilized with more or less commercial success. It is commonly assumed that the technical principles involved are quite simple and their application to a particular case easy. If these assumptions were true, we should anticipate a long list of uniformly successful leaching operations, which is not the case, and one would be justified only in calling attention to either unique or peculiar features of any particular enterprise; whereas, in studying the problems of the recovery of copper from the old workings of the Ohio Copper Co. in the light of available descriptions of other leaching projects, we have not found the assistance hoped for to guide us to the best realization of our own opportunities. It appears desirable, therefore, to call attention to these guiding principles, together with a description of the facts of accomplishment.

Justification lies in the fact that the leaching and precipitation of copper at the Ohio Copper Co. mine in Bingham Canyon, Utah, is successful. This success is measured by an average monthly production of 600,000 lb. of copper at an average operating cost, to date, of 3.85 cents per pound at the company's workings, or 6.32 cents per pound after paying shipping and smelter charges on the finished copper. A total of 17,076,099 lb. of copper had been shipped to the smelter from the beginning of operations, August, 1922, to April 1, 1925. Probably these results can be bettered with further study and realization of the factors involved and the devising of methods of meeting them. It is now an assured fact that the enterprise will have a relatively long and continuously profitable life and that its reserves will not, nor cannot, be suddenly and permanently depleted.

It is particularly noteworthy that the financing of this enterprise has been entirely from its earnings. The few hundred dollars necessary for the first experiments and production were obtained by the sale of used, and no longer needed, equipment from a mill belonging to the company; and all funds since required throughout the growth and development of the enterprise, from a few troughs with a production of 2000

32 RECOVERY OF COPPER BY LEACHING, OHIO COPPER CO. OF UTAH

or 3000 lb. per month to the present output, have come from receipts in hand.

It will be pertinent to quote here from a report of the General Manager to the Board of Directors, covering operations for the fiscal year 1924, as follows:

The total number of gallons of water treated in this period was 672,408,000, which is equivalent to 2,801,700 tons. The average copper content was 4.0302 lb. to the ton of water; and the total copper content, therefore, was 11,639,345 lb. The recovery, based on the daily estimates of the plant, was 11,290,165 lb. which represents 97 per cent. of the copper contained in the heads. In the tailing water was, therefore, 349,180 lb., and of this amount, we recovered, in the outside plant, 206,365 lb. making a total recovery in pounds of copper of 11,496,530 lb. and the amount lost in the tails was 132,815 lb. These two recoveries, both from the inside and the outside plant, show a recovery of 98.77 per cent. of the copper contained in the heads.

During the same period, our shipments to the smelter consisted of 18,127,200 lb. The average moisture content was 28.67 per cent., which made a deduction of 5,208,088 lb., leaving the dry weight 12,919,132 lb. The average copper content was 88.99 per cent. and the gross copper shipped to the smelter was 11,496,530 lb. The copper deduction made by the smelter was 381,201 lb., leaving the net pounds paid for by the smelter, 11,115,329.

The average price paid by the smelter was 12.876 cents per pound and the amount realized therefrom was \$1,431,217.26. The total cost per pound, including smelter charges, was 5.815 cents per pound; the operating profit for the period, per pound, was 7.061 cents; and the total operating profit therefrom, for the year, is \$784,759.56.

The total number of pounds of copper extracted from Jan. 1, 1923, to and including Dec. 31, 1924, is 15,546,873; and the total operating profit for this same period is \$1,048,840.43.

HISTORY OF OPERATIONS

In August, 1922, pumping was started, distributing 250 gal. per min. of water from Bingham Canyon Creek upon the surface of a large fill of broken rock overlying a portion of the caved zone. The solution reaching the Mascotte tunnel contained 0.45 per cent. copper, demonstrating that recovery of the copper values would be commercially feasible; the following January, the pumping capacity was increased to 400 gal. per min. At that time, the copper was precipitated in a row of boxes, using "country scrap" or whatever iron was available locally. These facilities were inadequate and insufficient, but results were soon sufficient, financially, to permit of a widening of the Mascotte tunnel and the installation therein of two rows of launders of improved design, one on each side of the haulage track; a larger and more efficient precipitation was promptly realized with improved profits. In the spring of 1923, with the installation of a larger pump, the water was increased to 600 gal. per min. In November, 1923, water from the Bingham Mines became

available, which, with a reuse of a portion of the tailing solution, gives a supply of 1200-1400 gal. per min. at the surface, delivered by a relay system of pumps.

The leachings reach the Mascotte tunnel through some one or other of the old ore chutes, depending on where it is applied at the surface, and is laundered to the precipitation boxes. In the earlier operations, leakage losses were serious; these losses were stopped by guniting the precipitation launders.

Production in January, 1923, was 120,000 lb.; in October of that year it had reached 351,801 lb., the recovery having increased from 41.9 to 99.2 per cent. For 1924, the production was 11,496,530 lb. of copper, a recovery of 97.3 per cent., and the copper content of the product shipped from Lark averaging 88.99 per cent.

Early in the operations, it was recognized that the "country scrap" was an inefficient precipitant. Since June, 1923, a detinned scrap iron prepared by the Metal & Thermit Corp'n. in California has been used; this has proved highly efficient, more than justifying the greater initial cost.

THE OREBODY

The orebody of the Ohio Copper Co. has recently been described in detail in publications of Varley, Oldright, and Wormser.¹ The veins, on which mining operations originally depended were more or less completely worked out and the original stopes and intermediate regions broken down, so that the property now consists of a "caved area," or more properly, a zone of broken rock surrounded on the sides, bottom, and much of the top by consolidated or mainly unbroken rock. The caved zone may be roughly described as a truncated cone, distorted, inverted, and standing at an angle of about 40° from the vertical. It is thought to be quite completely and uniformly filled with broken material of approximately 4 in. diameter on the average. The upper transverse dimensions of the cone are approximately 1400 by 600 ft. The axis of the cone is approximately 1200 ft. and the zone is estimated to contain 38,000,000 tons of rock. The truncation of the cone at the bottom has about one-fourth the area of the top, is horizontal, and from it chutes lead to the Mascotte tunnel, about 700 ft. lower. All this material carries copper, both in the caved zone and the surrounding consolidated rock. A vast number of assay figures on the old maps of the company give 0.88 per cent. as the average; but an inspection of these assay maps suggests a higher figure as more probable. The assay of the heads at the

¹ Address by Varley and Oldright, Bureau of Mines, before Utah Metal Mining Institute, Salt Lake City, May 5, 1923; Oldright, *MINING AND METALLURGY* (1923), 4, Pages 1-4; Wormser, *Eng. & Min. Jnl.-Pr.* (Oct. 20, 1923) and (July 26, 1924).

mill formerly operated by the company averaged 0.88 per cent., hence this figure is regarded as the most reliable.

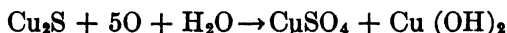
The rock itself is a porous quartzite, or sometimes a monazite, easily crushed or shattered, with sulfides of copper or copper and iron irregularly disseminated, sometimes in streaks or stringers, more often in small particles, always with more or less evidence of copper sulfate on surfaces and frequently malachite and azurite.

The original mineral, which alone concerns us, is chalcocite Cu_2S , as it has been shown by Zies, Allen and Merwin² that, at temperatures below 200°C ., the reactions between the various sulfides of copper, iron, zinc and lead with copper sulfate yield chalcocite as the final stable phase persisting. These facts may be summarized conveniently, as follows:

Pyrite (FeS_2) \rightarrow covellite (CuS) \rightarrow chalcocite
 Pyrohotite (Fe_7S_8) \rightarrow chalcopyrite (CuFeS_2) and bornite (Cu_5FeS_4)
 Bornite (Cu_5FeS_4) \rightarrow chalcocite (Cu_2S)
 Chalcopyrite (CuFeS_2) \rightarrow covellite (CuS) \rightarrow chalcocite (Cu_2S)
 Sphalerite (ZnS) \rightarrow covellite (CuS) \rightarrow chalcocite (Cu_2S)
 Galena (PbS) \rightarrow covellite (CuS) \rightarrow chalcocite (Cu_2S)
 Covellite (CuS) \rightarrow chalcocite (Cu_2S)

It is possible that at some particular time or spot one or more of these other minerals might be present as well as chalcocite, but sooner or later they will disappear with the formation of the last. It is also possible that gold, silver, arsenic, antimony, lead, zinc, nickel, cobalt, bismuth, etc., might be present.³ We are without confirming evidence as to these, at least in significant amounts, and the only solutes appearing in leachings of this ore are copper, iron, magnesium, calcium, sodium, aluminum (as Al_2O_3), silicon (as SiO_2), sulfur (as sulfuric acid).

Chalcocite, Cu_2S , is quite readily attacked by oxygen at ordinary temperatures in the presence of water, and whatever reactions may intervene, the result may be summarized in the equation:



The reaction is markedly exothermic, hence will proceed with rising temperature and increasing acceleration, provided it is not retarded or checked by: (1) Cooling, (2) exhaustion of the supply of oxygen or water, (3) accumulation of too high a concentration in the resulting solution of the soluble reaction product, CuSO_4 ; (4) mechanical interruption by formation of a protecting film of the insoluble hydrate.

² *Econ. Geol.* (1906), 11, 407; see summary by Clark, *The Data of Geochemistry*, U. S. Geol. Sur. (1924) *Bull.* No. 770, 673, 676.

³ See Analysis of Finished Copper, by Wormser, *loc cit.*; an analysis of the waste liquor from the portal of the tunnel at Lark is in the records of the University of Utah, showing the presence of these same constituents.

Each of these factors is of primary importance and must be given full consideration in determining that procedure in applying water and air to the orebody, which, in the summation of their effects, will make this summation a minimum. They will be discussed in detail later, but are cited here to emphasize the importance of the characteristics of the rock material forming the orebody.

It has been pointed out by Oldright that the quartzite and the quartzite-monazite host, carrying the disseminated sulfides of copper or mixed sulfides of copper and iron in this deposit, are rather readily permeable to water. Not only is this true of cleavage cracks and parting planes, but, to a marked degree, throughout the consolidated rock mass. This is readily proved by soaking a weighed piece of the rock in water. When taken from the water, after the surface is wiped dry, it will be found to have markedly increased in weight (different pieces, however, naturally showing wide variations in the percentage of absorption) and, on drying, there will practically always be more or less of a deposit of copper sulfate on the surface. This procedure can be repeated many times with the same piece of rock, each time bringing copper sulfate to the surface.

The marked absorbent character of this rock material makes it apparent that we are concerned here not only with the copper appearing in appreciable cracks and crevices or surface coatings, but with the entire mass of disseminated copper minerals. The water absorbed so readily must be mainly in very thin layers, or films; whether in layers of molecular dimensions, as held by some authorities, or thicker, need not now concern us. It is of the utmost importance, however, to remember water has a selective power of absorption for gases and will absorb from air relatively much more oxygen than nitrogen. More important yet, in thin layers or adsorption films, the water appears to be, or actually is, under great pressures so that it absorbs many more times the oxygen than it would in ordinary circumstances; that is, today there is a great increase in the solubility of oxygen in film water. We do not suggest that the film water inside a wetted rock mass is saturated with oxygen; probably the mass is far from saturation, but it is very probable that if the individual rock masses are bathed with film water, instead of large masses, a much larger amount of oxygen will be carried into the rock masses than would otherwise be the case, and under the most favorable conditions possible for a continued oxidation of the contained minerals. In other words, a rationally controlled leaching operation in an orebody, such as that of the Ohio Copper Co., will continue to form as well as remove copper sulfate. Two practical consequences are apparent. The life of the enterprise is not determined by the amount of "soluble" copper present at any particular time, and it is not physically possible suddenly and completely to deplete the ore reserve. Should this be attempted, very certainly, and probably quite quickly, the

mine would again be prepared to yield satisfactory returns to a rational operation.

Copper sulfate, being a salt of which the base is relatively less strong, that is less ionized in aqueous solution than is the acid, the solution of this salt will have the properties of an acid solution and will dissolve copper oxide or hydrate. Hence, a solution percolating through such an orebody as we are considering must become acid, at least beyond the layer of application, and dissolve copper hydrate, which is one of the immediate products of the reaction between chalcocite, air, and water. The normal salt, *chalcanthite*, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, according to Clark,⁴ is deposited by evaporating cupriferous mine waters. He quotes a reported case in Chile, when *chalcanthite* is found as an impregnation in partly decomposed granitic rocks, associated with malachite, azurite, and chrysocolla. It has been our observation that the characteristic blue crystals of the normal salt, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, can be obtained from a laboratory evaporation of the leachings, but the surface coatings in the mine and plant workings more often have a greenish color and the general appearance of the basic salt, *brocanthite*, $\text{Cu}_4(\text{OH})_6\text{SO}_4$. We have not attempted to prove the presence of *brocanthite* in any particular case, for it would have but an academic interest, and there is good reason to think the coatings we observe are of a wide range of basicity with *brocanthite* a special case somewhere within this range. It will be interesting to determine, when opportunity serves, whether or not we are dealing here with one or more series of solid solutions. The fact is that leaching these products, either with pure water or a slightly alkaline solution, removes the acid more quickly than the base; and if the process is several times repeated, there is a moist insoluble mass that then absorbs carbon dioxide to form malachite, $\text{Cu}_2(\text{OH})_2\text{CO}_3$, or azurite, $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$. Both these basic carbonates are found in the ore masses in the caved zone. They were most probably formed at times when this material was at or near the surface or in relatively dry workings of the old mine, for it is inconceivable that they could form in the presence of a solution of sulfuric acid. In fact, they are more or less readily dissolved by the leachings and are a part of the "soluble contents" of the orebody.

Of the other components (mineral species) or constituents (elements or radicals) in the orebody, iron alone seems at this writing to have any practical importance. Laboratory investigations on leaching the ore continuously with distilled water and with dilute acid solutions show iron to be removed continuously as well as copper; these observations are in harmony with those on the large-scale leaching of the caved zone. This leached iron is partly ferrous, partly ferric, indicating as origin not only sulfides but silicates and that leaching of the orebody will produce a

⁴ Data of Geochemistry, U. S. Geol. Surv. (1924) *Bull.* No. 770, 678.

continuous degradation and disintegration of the orebody as well as decomposition of some of its components, which makes for a greater porosity and ease of removing copper. Its greatest importance lies in the possibility that it may form protective coatings of ferric hydrate, inhibiting the action of the percolating waters, and that it may affect the operations in the precipitating launders.

LEACHING

The leaching of a soluble substance, uniformly dispersed through a more or less uniform absorbing medium of small-pore dimensions, is a process that has been rather well studied. In the absence of disturbing factors, it is described by the equation:

where x represents the amount that has been leached for a given interval of time; gallons of water leached, or whatever standard of reference may be desired, represents by y ; k , is a constant, characteristic of the particular absorbent; and A represents the total amount of the soluble substance that can ultimately be recovered by leaching.⁵ The corresponding graph is an hyperbola symmetric to the axis of abscissas. Usually, the disturbing factors are changes in the specific adsorptive capacity of the insoluble medium for the solute with concentration, hydrolysis of the solute, flocculation or deflocculation of the absorbing medium; phenomena that are disturbing only when the leaching has proceeded to a point when the value for x has more or less closely approached the value A . For various other reasons, mechanical and financial, it is seldom worth while to attempt a complete recovery of a soluble substance by leaching. Usually, also, it is comparatively simple to make a few experiments to discover the values of k and A with sufficient accuracy; the formula then becomes really useful for describing or predicting the results of leaching. One can determine, for example, with a desirable approach to accuracy, the amount of water that will be required and the time required, or the "life" of the project.

Unfortunately, no such simple treatment of the problem of leaching the orebody of the Ohio Copper Co. is practicable, because of the disturbing factors to be now noted; but it is deemed desirable to present this method of approaching the problem as well adapted to bringing into consideration the nature and importance of the disturbing factors and as emphasizing that the recovery of copper from this orebody by leaching

⁵ This is the well-known formula for reaction velocity, whether chemical, physical, or biological. It has been extensively used in leaching studies. For early examples see publications of the Bureau of Soils, U. S. Department of Agriculture.

is not, and cannot be from its very nature, a rapid procedure; rather it is a time-consuming one, probably of many years.

The interstices of the orebody in the caved zone, where most of the leaching has been done, are large and irregular, compared with the capillary surfaces in the individual pieces of rock. The percolating waters bathe the surfaces only of the individual masses, whereas most of the soluble copper is within the fine pores of these individual masses, from which it can diffuse but very slowly, compared to the rate of flow of the percolating water. Moreover, copper is continually being converted to soluble sulfate in and upon these masses and at continually varying rates. It is impossible to determine, or predict quantitatively, how these simultaneous phenomena will mutually affect the composition of the solution at any given time or position within the orebody, and hence to make use of a quantitative formula for computing the removal of the copper by leaching. Even more difficult is it to evaluate to the consequences of the differences in rate of solution of the several copper compounds, with the rate of percolation of the water. It is well recognized that a slow percolation in thin water layers is the most efficient use of the given volume of water. However desirable it may be that the percolating waters flow over the individual ore masses in film form only, it can hardly be anticipated that this state of affairs will ever be attained completely, and it certainly has not up to the present, for its importance has not been fully realized. It has been recognized that the distribution of a given amount of water over a large area in small streams is preferable to a concentration in a few large streams, hence the use of perforated launders.

Within the past few months the problem of the best distribution of the water has been closely studied and in the light of large-sized practical experiments. The water has been delivered in large streams into holes on the surface, into cracks, and fissures; upon a rather wide area prepared by deep blasting (20-30 ft.) under the overlying burden of soil and into consolidated rock adjacent to the caved zone, as well as upon the surface overlying the caved area in well-distributed volumes. As well as can be determined, it has been found that there was but little percolation of the water throughout the consolidated rock and, while there was a recovery of some copper, the heads were disappointingly low. Better results were obtained from the water entering by way of holes over the caved zone; but the best results came from a wide distribution over the caved zone. It is now planned to abandon temporarily efforts to leach the consolidated-rock regions pending the inauguration of a systematic procedure for preparing this region for leaching, and to confine the leaching operations to the caved zone for the immediate future. To this end, a tunnel (Dederich on 100-ft. level) is now being driven through the upper part of the caved zone from which laterals and sub-laterals will be constructed so that, when completed, practically the

whole horizontal cross-section of the region or any desired part of it, can be wetted at once, thus permitting a desirable mobility in alternately leaching and drying. The completion of this tunnel system will make possible the leaching of a much larger part of the caved zone than has been practicable. In fact, it is reasonably certain that a relatively small part only of the broken mass has been leached and that far from thoroughly.

The percolating waters have two dominant duties, as well as several minor ones. They must dissolve copper sulfate and carry it to the precipitating plant; and they must carry oxygen from the surface for the continuing oxidation of the sulfides of copper within the ore mass. Both these functions are dependent on the manner of applying the water; and there is a decided division of opinion on this fundamental operation. It is held that mass percolation, where a large volume of water is applied quickly to a restricted area, by bringing a large volume of water in a given time into contact with the copper-sulfate coatings on the individual rock masses, dissolves them more completely; and that this method of application traps and mechanically drags into the orebody large volumes of air. To these views it can be objected that a relatively large part of the water is passing through the large interstices out of contact with the copper sulfate, and having no appreciable effect upon it; that the rate of solution of crystallized salts is so slow, compared to the rate of passage of the water being forced past it, that the solvent action effected is out of all reasonable proportion to the volume of water required for it; and that it is improbable that any large part of the trapped air is carried very far, being pretty thoroughly scrubbed out by the first few feet of broken rock, and returns to the surface without doing any useful work. Obviously, this method requires the maximum amount of pumping.

Diametrically opposed is the view that the water should be applied in the film form, or as nearly in the film form as can reasonably be attained in a practical operation, which means distributing any given volume over a very wide area slowly but continuously. In this way, the water (for the most part at least) will enter and continue through the orebody in approximately film form, a very much larger area of ore surface will be bathed, and a larger amount of copper sulfate will come into contact with it and a much longer time for solution will be afforded. A much larger amount of oxygen (in distinction to air) will be absorbed by the films at the surfaces and carried in dissolved form far into the interior of the orebody and in the form most useful for oxidation of the minerals.

It should be noted that spreading the water over so large a surface as to attain film form induces a rise in temperature, especially when the surface being wetted is relatively dry. An increased temperature above that of the entering water can be maintained by making the percolation

sufficiently slow. It has been pointed out that a high temperature is favorable to the rapid oxidation of the copper sulfides, from this point of view a film percolation is to be preferred.

Copper sulfate in aqueous solution is hydrolized, the solution behaves as though it contained free sulfuric acid and will dissolve copper hydrate. The greater the concentration and the higher the temperature, the greater will be the amount of the hydrolysis and the more copper hydrate will be dissolved. Similar statements hold for the action on copper carbonates. Likewise, the solution will dissolve the hydrates of iron, which are practically always an accompaniment of the oxidation of copper sulfides in nature, and by forming protecting films may retard the action. Obviously, as film percolation rather than mass percolation tends to dissolve and remove more copper and iron hydrates from the sulfides, it is to be preferred.

The film method of percolation is to be preferred to mass percolation from every point of view, especially because it will bring more copper to the precipitating launders daily, or for a given volume of water, and also because it better promotes the conditions in the orebody favorable to the continued and rapid production of soluble copper sulfates.

The time required for penetration of the caved zone by water applied in the mass percolation manner, as measured by its appearance in the launders in the Mascotte tunnel is about 48 hr. If, however, film percolation is followed, this time element will be longer (probably very much longer) depending on how near to the ideal film condition the practice may be. No sufficient knowledge exists of the various factors that particularize this case to justify any attempt at evaluating them; consequently it is useless to attempt any theoretical estimates of what this time will be. It may well be two or three weeks. Probably for a short interval, the first runnings will be pure or nearly pure water, but quickly high "heads" will be attained, which will persist for a relatively long period and then gradually diminish. Obviously, once the flow is established the volume delivered to the precipitating launders for a given interval of time will be the same, no matter what system is followed, and independently of the rate through the ore mass.

Considering, now, an individual piece of the ore, over the surface of which the percolating water is moving, the water with dissolved oxygen penetrates more or less completely the entire mass; reaction with the contained sulfides sets in, and if not checked by too rapid a flow of cold water on the outside, a quick rise in temperature follows; the reaction proceeds at constantly increasing speed for awhile, and then gradually slows down as there is an accumulation of the reaction products. If the soluble products of the reaction be removed as they are formed and the undissolved products do not form a too impenetrable coating, the reaction continues until the sulfide mineral completely disappears—or what is

more likely, the supply of oxygen is exhausted. The temperature may rise to the boiling point of water, introducing another factor in percolation with which to contend.

However, diffusion of the reaction products from the interior of the mass through the capillary and film water to the flowing water on the surface of the mass is very slow and cannot add much to the content of the percolating water, at least in any individual case, although the aggregate be appreciable; consequently, the reaction slows down and stops. If the percolation is stopped and the clearly washed surface of the mass dries, evaporation at the surface begins; there is a capillary flow started from the interior to the surface that carries with it the dissolved sulfates, which will be deposited on the surface as evaporation proceeds as a more or less thick and dense film of basic copper and iron sulfates, with less conspicuous amounts of other substances in individual cases. How far, or rather how long, this procedure should be carried, in practice, is purely a matter of judgment of the operator at present. The movement of water, or of a dissolved substance, in a porous medium follows a law expressed by the formula $y^n = kt$ where y is the distance and t the time.⁶ The value of n is constant for any given absorbent medium, say an individual piece of rock, but the porosity appears to vary too much in different pieces, as well as the size of the different pieces, to permit any useful application of the formula.

On resumption of leaching, water again penetrates the ore mass, carrying a new supply of oxygen, for the reaction with the remaining sulfides, and sulfuric acid for the solution of protecting films of hydrate. Thus, the cycle of operations can be continued indefinitely, but with slowly diminishing results until that time when it will be of no practical importance. It would be advantageous to know how far the phenomena just described have progressed in our orebody, particularly in the caved zone. The driving of the Dederich tunnel and laterals affords an unusual opportunity to obtain samples to test this matter and accumulate data of great technical value, not alone for the Ohio Copper Co.'s enterprise, but for all copper-leaching projects.

The laboratory problem is to determine not only the total copper in the sample, but that proportion of the total which is now soluble in water and soluble in dilute sulfuric acid. It is proving to be far from a simple problem. As a preliminary step, a column of broken ore was arranged by placing about 4500 gm. of rock from the broken zone in a series of funnels made by cutting off the bottoms of "Winchester quarts," or the ordinary bottles in which acid is sold. The funnels were arranged

⁶Cameron and Bell: *Bur. of Soil, U. S. Dept. of Agriculture Bull.* No. 30, 50 *et. seq.*, 18.

Bell and Cameron: *Jnl. Phys. Chem.* (1906) 10 659; Wolfgang Ostwald, *Zeit. Kol. Chem.* 2, Supplementheft, *Zeit. Kol. Chem.* (1908), 20.

one above the other so that the drip from one would fall upon the ore in the next funnel below and in such a manner that it would splash over the whole surface and percolate throughout the entire contents of the funnel. About 7500 cc. of distilled water were thus percolated through the entire column, the operation taking approximately 4 hr. The collected drainings were then sampled for analysis and the residue again percolated through the column. This operation was repeated twenty times; the concentration of the percolate, with respect to copper, increased with each cycle from 0.0442 per cent. after the first cycle to 0.113 per cent. after the twentieth, when the series of cycles was interrupted. The final solution contained 0.0032 per cent. ferrous iron and 0.006 per cent. ferric iron.

At the same time, working with Dr. Thomas B. Brighton at the University of Utah, a sample taken from the Dederich tunnel was crushed to $\frac{1}{4}$ in. or less and then carefully quartered and a subsample weighing 123 gm. was placed in a Soxhlet apparatus, thus subjecting it to continuous percolation with warm distilled water. This operation was repeated with successive portions of water at approximately 2-hr. intervals and the resulting solutions analyzed for copper. Copper was leached in progressively diminishing amounts for five successive extractions, the total aggregating 0.2231 per cent. While copper could yet be extracted by water, the amount in the last extraction was sufficiently low to justify interruption of the procedure.

As sulfuric acid is not appreciably volatile with steam, a moderately dilute solution of hydrochloric acid was used in the Soxhlet assembly and successive extractions analyzed for copper, the results aggregating 0.234 per cent.

Finally, the solid residue was removed from the instrument, the coarser particles further comminuted and the copper yet remaining, and amounting to 0.388 per cent. of the total sample, was recovered by digestion on a hot plate with nitric acid. Therefore, of the 0.795 per cent. in this sample, 0.457 per cent. was taken out by water and dilute acid, indicating a possible recovery by leaching of 57 per cent. of the copper present, even though no further oxidation should take place.

The importance of these experiments lies in the confirmation they afford to the *a priori* considerations stated above; that the leaching of copper sulfate from this orebody must be continuous over a long period of time; that formation of copper sulfate is in progress; that the copper hydrate being formed simultaneously will be recovered by the acid percolating solutions, but that neither operation is, in itself, a satisfactory procedure for the daily laboratory analyses of a number of samples, being time and labor consuming and, generally, cumbersome.

The water available at present for the leaching operations of the Ohio Copper Co. has two sources. The company has an agreement with

the town authorities of Bingham and all other interested parties to pump 400 gal. per min. from the open drain through that town, returning an equal volume from its tailings; this is called the creek water. It is always acid in character, contains considerable organic matter, which is objectionable as a consumer of oxygen, and varies in composition from time to time. A typical analysis is given in Table 3. The pumping operations at the Bingham mines are interrupted at 45-min. intervals, however, so the average from this source is about 600 gal. per min. It is anticipated that this source of supply will be largely augmented in the near future. The water at present has an alkaline reaction due to dissolved carbonate of lime. It is quite constant in composition and a typical analysis is shown also in Table 3. We are without adequate information as to its probable composition when the augmented supply becomes available.

To these must be added the tailings from the precipitating launders, which are quite acid in character and carry large amounts of dissolved iron. At present, part of these tailings are discharged through the Mascotte tunnel to Lark, where the small amount of copper they sometimes carry is precipitated on iron scrap in a "scavenger" plant. Another part is mixed with the Bingham mines water. When these waters are brought together, there is a noticeable precipitation of ferrous hydrate or carbonate. Passing through the pumps, through 1600 ft. of piping to the surface, and through the launders, pipes and ditches on the surface, the precipitation continues, accompanied by absorption of oxygen, so that all the conduits are soon lined and the surfaces upon which the water is discharged are soon covered with a deposit of ferric hydrate. On standing, the ferric hydrate settles to a dense mass, which has much merit as a seal in the pipes and launders, but is otherwise a great nuisance.

TABLE 3.—*Analyses of Waters Used for Leaching*

	Creek Water, Per Cent.	Bingham Mines Water, Per Cent.	Recirculated Water, Per Cent.
Fe".....	0.016	0.001	0.107
Fe'".....	0.012	0.001	0.005
Cu.....	0.0016	0.0024
CaO.....	0.033	0.029	0.047
MgO.....	0.020	0.006	0.021
H ₂ SO ₄	0.006	0.008
CaCO ₃	0.010

When the tailings and Bingham mines waters are mixed, both the dissolved calcium bicarbonate and the ferrous sulfate are greatly diluted; unfortunately, at high dilutions, the reaction between these salts is very

slow, probably because of the very slow disengagement of the carbon dioxide. A laboratory investigation showed that about equal volumes of Bingham mines water and tailings produced a neutral solution, but after pumping air through such a mixture for intervals of about an hour, no apparent precipitation was obtained although it is readily apparent at all times about the mine workings. A precipitation was gradually obtained in the laboratory by heating such mixtures. Very serious consideration is being given to this "iron" problem, as it is undesirable to have the hydrate deposited in the orebody, even if it takes place at very shallow depths only; it adds appreciably to operating costs to replace piping the effective cross-section of which is reduced by the deposit. No chemical treatment seems to be economically justified. Filtration through sand seems to be the practicable and best means of meeting the situation. Not only will the solid precipitates be retained mechanically, but sand is particularly efficient in selectively absorbing iron from its dissolved salts and permitting the freed acid to be carried on by the percolating waters.⁷ This remedy, to be fully effective, presupposes complete adoption of the film method of percolation and practical engineering difficulties may prevent this being done in its entirety until the completion of the Dederich tunnel.

If, and when, the sand filtration method cannot be followed, it would be desirable to discard all the tailing waters, for their content of copper (about 0.4 lb. per 1000 gal.) is not sufficient to justify any treatment other than at the company's scavenger plant. Unfortunately, this is not deemed practicable at present, as it appears unwise to leach with the Bingham mines water directly, for it is feared that in the first part of its path through the orebody, it will precipitate copper instead of dissolving it because of its alkaline character. A mixing with the tailings is apparently the cheapest and an effective method of giving the percolating waters an acid reaction from the start of the leaching operation. Further experimental study of the question is under way.

Confusion regarding these "iron" phenomena has developed wherever similar operations are carried on and has led to erroneous concepts of what may be occurring within the orebody. It is assumed that ferrous sulfate is hydrolized in solution, which is true; that oxygen is absorbed and converts the hydrolized ferrous hydrate to ferric hydrate, which is true; and that the ferric hydrate then precipitates, which is not true, as any one may quickly learn by trying the experiment under controlled conditions of the laboratory. The total content of sulfuric acid is not changed on the absorption of oxygen and ferric sulfate is much more

⁷ For a discussion and references see Bureau of Soils, U. S. Department of Agriculture (1905) *Bull.* No. 30.

soluble than ferrous sulfate; consequently, there is no change in the content of dissolved iron. What does happen, if time and oxygen are sufficient, is a complete conversion of the ferrous sulfate to ferric sulfate and this latter is hydrolized to the degree that the solution behaves in its solvent action on metals, oxides, or carbonates, as though it were a solution of free sulfuric acid. If, now, the solution is neutralized by adding some relatively strong basic substance, as the calcium bicarbonate of the Bingham mines water, the weak base ferric hydrate will be formed and, being insoluble, it will precipitate. The descriptive phrase "hydrolyzing out of iron" is most unfortunate in concept and expression. The phenomenon of hydrolysis of electrolytes in aqueous solution is entirely different and distinct from the phenomenon of precipitation of an insoluble substance resulting from a reaction and there can be no justification for confusing the two.

Ferric hydrate is an exceedingly weak base, weaker than cupric hydrate which, in turn, is weaker than ferrous hydrate. If, then, to a given solution of ferric sulfate, cupric hydrate or ferrous hydrate is added slowly and continuously, at first there will be solution and disappearance of all solid phases, but in time ferric hydrate will commence to separate as solid phase, just as though any other base were being added, such as magnesium hydrate or sodium hydrate. As pure ferrous hydrate will turn red litmus to blue,⁸ one would expect that a complete precipitation of ferric hydrate might be accomplished by adding enough ferrous hydrate, although obviously more than a stoichiometrical equivalent of magnesium or sodium hydrate, because ferrous sulfate itself is appreciably hydrolized with formation of an acid solution. Similarly, ferric iron may be precipitated from a sulfate solution by cupric hydrate. The precipitation of cupric hydrate by ferrous hydrate is a more complicated affair because of the difference in the state of oxidation; it is to be expected that there will be reduction of the cupric to cuprous hydrate with oxidation of the ferrous to ferric hydrate and precipitation of this last.

It has been shown above that cupric hydrate and ferrous hydrate are present in the orebody. It is conceivable that a percolating solution of ferric sulfate, either in traversing a long path or by moving slowly, might ultimately dissolve sufficient cupric or ferrous hydrate to cause precipitation of ferric hydrate, especially if this path had previously been scoured free from cupric sulfate. The probability of such a catastrophe seems remote, but catastrophe it might well be if the precipitation were long continued, hence, the wisdom in not taking the chance and removing the possibility. The only certain and practical way yet suggesting itself is the use of the sand filter.

⁸ Mendelew.

PRECIPITATION

The precipitation plant is located in the Mascotte tunnel about 2 miles from the portal at Lark. It is arranged in two rows of launders on either side of the haulage track, each row aggregating 1600 ft. in length, or 3200 ft. in all. The rows are subdivided into sections of 320 ft. with a siphon at the end of each section to bypass the pregnant solution to the opposite row during washing or loading operations. The individual units are 16 ft. long with a cross section 32 by 32 in. They are gunited to prevent leakage. A false bottom is supported 17 in. above the floor of the launder; this bottom is a wooden lattice with $\frac{1}{4}$ -in. square openings and is built in sections for ease of handling. Immediately above the lattice, in the side of the launder, is a hole that is opened during washing or draining; at other times it is closed with a plug. The rows are set with a grade of 0.5 per cent. The pregnant solution (heads) is brought to the launders from the old ore chutes, where it appears in the tunnel, by a launder system aggregating about 1500 ft. The barren solution (tails) is discharged to a drain through the tunnel to Lark, but with a gate a few feet beyond the precipitating launders, where it is diverted, in part, into a sump from which it is pumped to the surface above the orebody. This sump receives also the Bingham mines water in transit to the surface.

The scrap, or detinned iron, is received in compressed bales weighing about 75 lb. each. The Metal & Thermit Corpn., from whom it is obtained, remove the tin by treatment with caustic soda, leaving a metal with a surface very well adapted to copper precipitation. Usually it reaches the launders in excellent condition, but sometimes there is a little adherent caustic and rust. The bales are torn apart at the launders and the loosened scrap heaped upon the false bottom; it is the duty of the plant operatives to keep a full supply in the launders always. It seems to be necessary that the scrap be piled well above the surface of the solution and apparently offering an excellent opportunity for rusting; twice the equivalent iron is lost as a copper precipitant, and with added contamination of the copper. The experiment was tried of running two series of boxes in parallel; in one series the scrap was kept completely submerged, while in the other it was piled above the surface as usual. After some days the copper precipitated was sampled. They showed no significant difference in grade or iron content but in both cases were somewhat above the grade usually recovered from the same boxes. The latter fact is probably due to the more than usual interest, and therefore care, of the plant operatives in the experimental boxes. It is probable that if solid oxides of iron were formed, they were floated on to succeeding launders. As the weight of scrap used and copper recovered were not recorded, it is yet to be determined if complete submergence is desirable or would justify the additional labor that would be required.

The Mascotte tunnel and all offsets where men are employed are well lighted by electricity. Extra and ample lighting is provided in the precipitation plant. An electric tram provides adequate haulage facilities and the ventilation in the plant is good. At intervals, 2-in. piping with hose attachments are provided for washing the copper and keeping the equipment clean. The equipment is first class and adequate, and the operations well done, due, in great measure, to the small labor turnover. Three shifts of fifteen men each are employed in the plant operations.

The pregnant solutions reaching the head of the launders vary somewhat in volume, from 1200 to 1500 gal. per min. The average rate of flow or advancement down the launder system is about 40 ft. per min., so that the minimum time of contact with metal is not less than 40 min. The gradient being fixed, the rate of flow is determined by the volume of solution handled and the effective cross section of the launders; this last, in turn, is determined by the amount of scrap submerged. The general policy is to crowd the submerged scrap as much as possible without causing overflows. Under any conditions, the velocity of transport is higher than the usual practice elsewhere, but it is thought to be an important factor for the production of a high-grade copper precipitate.

The composition of the pregnant solution also varies somewhat, and probably always will. Naturally we may anticipate much higher heads as development at the surface makes possible a wider area of ore surface to be bathed by the percolating waters; it is thought that this will be advantageous not only in an increased production, but because increases in grade of product and efficiency in iron consumption are promoted by "high" heads. The composition of the solution for the last six months of 1924 is indicated in Table 4, the figures being averages of the daily analyses.

TABLE 4.—*Pregnant Solutions for 6 Month Period, 1924*

Month	Head, Gal. per Min.	Insol., Per Cent.	CuSO ₄ , Per Cent.	FeSO ₄ , Per Cent.	Fe ₂ (SO ₄) ₃ , Per Cent.	CaSO ₄ , Per Cent.	MgSO ₄ , Per Cent.	Al ₂ (SO ₄) ₃ , Per Cent.
July.....	1352	0.011	0.494	0.052	0.147	0.141	0.102	0.168
August.....	1402	0.012	0.477	0.035	0.125	0.141	0.087	0.332
September.....	1343	0.013	0.454	0.060	0.086	0.141	0.097	0.157
October.....	1260	0.013	0.617	0.095	0.125	0.143	0.135	0.157
November.....	1324	0.012	0.412	0.049	0.150	0.148	0.197	0.077
December.....	1407	0.012	0.324	0.033	0.168	0.156	0.281	0.107

These figures appear to show that the use of the smaller volume of water not only brings higher heads to the precipitating launders, but also more copper. For instance, in October, with an average volume of 1260 gal. per min. percolation, about 65 lb. per min. of copper sulfate was

treated; while in August, with 1402 gal. and in December, with 1407 gal. per min., 56 and 39 lb. of copper sulfate per minute were treated. The figure for August is associated with, and probably due to, the extraordinary concentration of aluminum sulfate. The figures are practical arguments for film percolation. Further, it appears that while the percentage of total iron in the smaller and larger volumes does not differ significantly, so that the actual mass will be less with less water, a significant difference does exist in the state of oxidation, a larger proportion being ferric iron, when the larger volume of water is employed. This means that more scrap will yield less copper when the larger volume is employed.

The average copper (Cu) content of the pregnant solution for the year 1924 was 0.204 per cent., that of the barren solution 0.0058 per cent.; hence the recovery was somewhat better than 97 per cent. This must be considered a very gratifying result when the iron consumption is also considered. The record of actual shipments confirms the calculated recoveries quite closely and mechanical losses are small.

The principal factors determining the rate of precipitation of the copper, aside from temperature, are the concentration of the solution with respect to copper and sulfuric acid.⁹ Consequently, the precipitation regularly decreases as the solution becomes impoverished in copper content, and the acidity is decreased by solution of ferrous iron. These facts are shown in Table 5, which has been computed from the analyses of the solutions entering at the head of the sections indicated.

TABLE 5.—*Percentage Recovery of Copper in Several Sectors; Averages for the Year 1924*

Average volume of pregnant solution, 1276 gal. per min.

Average copper per 1000 gal. pregnant solution, 17.031 lb.

Sections.....	1-2	3-4	5-6	7-8	9-10	All
Recovery.....	37.2	29.2	17.9	8.7	4.3	97.3

The relatively high velocity of the solution through the launders, and the agitation thereby produced, prevents occlusion or "sticking" of foreign substances in or upon the copper films as deposited. Moreover, it floats, or carries in mechanical suspension, the smaller and lightest particles from box to box. This flotation is selective, hence there is a marked and progressive segregation of ferric oxide in the lower launders. These facts have been charted, Fig. 1, where "grade" of the product has been plotted against percentage of copper in solution. As a matter of practice it has been found that a high velocity of the solution is more important

⁹ Iron does not precipitate copper from an alkaline solution but zinc does; these facts suggest that the high concentration of acid is desirable because of the more rapid solution of the iron therein.

than long-continued contact of metallic iron and solution. In the earlier operations, when the launders were set so that the movement of the solution was sluggish, poor recoveries were realized; but, the recoveries were promptly brought to their present high efficiency when the launders were brought to their present gradient.

The speed with which the copper is precipitated may be a practical factor in the purity, or grade, obtained, aside from mechanical inclusions in the film. Theoretical and *a priori* considerations would suggest a better copper with slow deposition from dilute solution. Actually, plant results seem to be opposed in that the best grade of copper is obtained with high heads and rapid deposition, the grade always falling below 90 per cent. when the concentration of copper in solution falls below 0.06 per cent. Whether or not slow deposition is undesirable for good plant precipitation and the plant observations are a confusion of other and masking phenomena, is of practicable importance and must be worked out under controlled laboratory conditions.

In its progress through the launders, the solution becomes progressively leaner in copper, but progressively dissolves iron to form ferrous sulfate. Ferrous iron is a fairly strong base, so the hydrogen ion concentration is rapidly reduced. Gaseous hydrogen escapes from the solution and precipitation of metallic copper slows down. There must be some absorption of oxygen as well as evaporation in the passage through the launders; this oxidation is reflected in a higher and higher consumption of iron per unit of copper precipitated. The concentration may reach the point where a basic ferrous sulfate will separate as solid phase; some observations in the plant indicate that this has happened, although the major part of it must have floated off in the tailings. It has been suggested that in the nearly neutralized solutions of the lower launders the relatively "strong" base ferrous hydroxide causes a precipitation of the relatively very "weak" base ferric hydrate formed by the absorption of oxygen and that this accounts for the accumulation of the latter in the copper recovered. In other words, metallic iron in a saturated solution of ferrous sulfate exposed to the air will completely disappear to form ferric hydrate and it is futile to attempt the recovery of a small amount of copper from such a solution. Technically the addition of more water and sulfuric acid is the answer; economically, the problem is whether a very high recovery of copper is justified, considering the iron consumption and equipment necessary. The answer may well vary for different installations and at the same installation with changing conditions in the price for copper, iron or labor.

At the Ohio Copper Co.'s plant, the consumption of iron in the several sectors is to be determined with the precision necessary to justify any modification of the present practice, which has been developed empirically. It is believed that contamination of the copper from precipitated

ferric hydrate is not serious, if it occurs at all, the ferric oxide in the lower grades being explained by the rust on the scrap, with selective flotation. In all grades, there is always some iron, usually an insignificant amount, in the form of minute undissolved fragments of scrap, and a decidedly significant amount in occluded and adsorbed sulfates which cannot be removed by washing with water alone.

The iron consumption for the entire operation is about pound for pound; that is, a pound of iron is dissolved for every pound of copper shipped. This result would probably compare favorably with those obtained elsewhere; nevertheless, a margin for improvement exists. It shows that about 88 per cent. of the iron is actually used in precipitating copper. Allowing 2 per cent. for rust and impurities, about 10 per cent. is used in reducing ferric iron to the ferrous condition. No great improvement in the plant practice appears possible, hence any increased efficiency in iron consumption must be sought in an increase in the ratio of copper to iron in the pregnant solution with improved percolation. That this will be realized, is indicated clearly by the history of this enterprise.

THE PRODUCT

Depending on its position, the concentration of the pregnant solution, and to less extent on other factors, the space below the false bottom of the individual launder becomes filled with copper in from 6 to 30 days. Always several launders are about filled at the same time. The solution is then bypassed, by the siphons at the head of the section, and when the flow has ceased the plugs are drawn in the launders to be emptied, the scrap washed by means of the hose, and moved to a convenient place. The copper is agitated and washed by means of the hose, settled, the supernatant solution of ferrous sulfate drained off, and the copper shoveled into lorries and carried to the loading station at Lark, when it is shipped to its destination. On the whole, the operation is efficient. Washing the scrap recovers copper from it and improves its surface for further use, but entails a certain risk of carrying small fragments of iron and other undesirable components into the copper. Possibly a diaphragm pump could advantageously be employed for loading the lorries. About three-fourths of the product, when dried, will grade 90 per cent. copper or better; the remainder, from the lower launders and containing much iron, grades sometimes to a lower limit of 60 per cent., but usually above 70 per cent. copper.

By the time the product is loaded at Lark, it has settled and much water has drained from it. As shipped, it carries about 30 per cent. water, which has somewhat lessened at destination where sampling for settlement analyses are taken. Meanwhile, oxidation has taken place, the bright characteristic metallic appearance has given way to a dull

brown or almost black. On drying, in preparation of the sample for analysis, a further and more extensive oxidation occurs, which may amount to 5 per cent. or more, so that a product which should grade 90 per cent. copper will grade only 86.5 per cent. This difficulty is a serious handicap in the marketing of cement copper and working out an equitable basis for settlements. Two problems are involved. One, the working out of a quick laboratory method of drying the sample, which will preclude further oxidation without reduction of any oxides that may already be present; attempts to dry the sample in an inert gas are promising. The second problem is to free the product from moisture before shipment, without at the same time oxidizing it.

To this end, it has been suggested that the product be dried in a current of stack gases, but it is necessary to use an excessive amount of heat to remove the moisture to the point where oxidation will not promptly set in and continue extensively unless stirring be employed; and with stirring, dust losses are high.

Melting has been proposed. The product is excellent, for no refining is needed, and it appears to be a simple matter to reduce copper oxide to a negligible minimum and slag and skim off the iron, sulfur and silica. But the dust losses are again high in the melting and the product must be dried first.

Recourse to briquetting at high pressures seems to promise a way out of the difficulty. The Salt Lake Iron & Steel Co. has put at our disposal 100-ton hydraulic press and the Salt Lake Shop of the D. & R. G. W. R. R. has permitted certain experiments with its 600-ton press.

The first experiments were made with rejects of the settlement samples, which were stirred up with an excess of water. The results were promising but the bricks were too high, in comparison with their cross-section, and broke or shattered too easily, generally along surfaces in which some foreign substance, usually a silicate mineral fragment, was embedded. On standing 24 hr., apparently due to readjustment of internal stresses, the bricks became much tougher and resistant to breaking tests. Coming from the press, the bricks felt cold, but quickly came to room temperature and appeared to be perfectly dry. The water extruded in the pressing carried notable quantities of ferrous sulfate and some ferric sulfate.

Bricks were then prepared at various pressures, up to 150 tons per square inch. The densities, when plotted against the pressures, fell on a smooth curve; but as subsequent investigation proved them to have no absolute significance, they are not presented. The curve was asymptotic and it appeared that the higher pressures would not be justified by the increase in density attained, considering the added expense of building a press for a quantity production with excessive pressures. At 150 tons per square inch, the plunger was bent and split and the die was distorted.

Special steels from two manufacturers have been secured, new dies and plungers made and tested, and it is no longer a problem to secure suitable material for them.

The brick made at 150-tons pressure, although distorted and, when tested, showing but little greater density than bricks made at half the pressure, nevertheless appeared, generally, to be more desirable and less resistant to abrasion than any yet made. The density, a little more than 6, was far short of the density of melted copper; hence a more detailed study of the bricks was made in various ways, which need not be detailed.

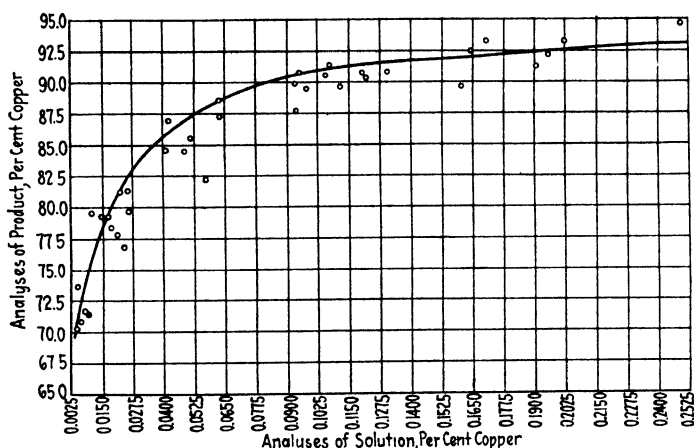


FIG. 1.—CURVE SHOWING GRADE OF PRODUCT OBTAINED USING VARYING CONCENTRATION OF COPPER IN LEACHING SOLUTION; ANALYSES OF PRODUCT OBTAINED FROM AVERAGE COPPER CONTENT OF CONTROLS RECEIVED FROM JUNE, 1924, TO APRIL, 1925; ANALYSES OF SOLUTION, AVERAGE ANALYSES DURING THIS PERIOD.

It was found that, for stability, the truncated cone is most desirable and that the height should be less than the diameter; the samples of copper tested so far were unsuited to the purpose, the individual particles being coated with an oxide film. A suitable die having been made, a barrel of the fresh product was shipped directly to the foundry, a brick made for the instruction of one of the laborers, who thereupon, himself, promptly made about 100 of the bricks, at a pressure of 40 tons to the square inch, without slip or mischance of any kind to bricks, die or plunger. This shows that the operation can readily be carried on by intelligent labor without special training; satisfactory steel is available for dies and plungers and excessive pressures are not required, for the bricks made were in every respect satisfactory. They were heaped promiscuously in a nail keg, which was placed in the tonneau of a small motor car and carried over roads and pavements, cartracks, etc., and showed no abrasion. They are very resistant to breakage on being dropped or struck with a hammer. They have been drilled and sawed,

showing clear metallic surfaces after the tool. After standing for several weeks, the surfaces are yet bright, showing little or no evidence of oxidation. Placed in a clay crucible in a muffle, they melt cleanly, as would a copper bar, without any suggestion of dusting. In fine, they appear to be in excellent form for shipping.

Analysis of the product shipped to the foundry was made at the plant laboratory, which reported a copper content of 91.4 per cent. Two of the bricks, picked at random, were sent to the laboratory which reported as follows:

	Cu, PER CENT.	Fe ₂ O ₃ , PER CENT.	INSOL., PER CENT.	S, PER CENT.	MOISTURE, PER CENT.
Before briquetting.....	91.48	1.90	0.70	0.27	43.80
After briquetting.....	94.43	1.64	1.00	.18	.76

Another brick, also picked at random, was sent to Crismon & Nichols, public analysts, who reported 95 per cent. copper. It may thus be said that an appreciable increase in grade is obtained by the briquetting in addition to putting the product into a dry form, resistant to oxidation, and well suited for direct shipment or to melting. Preliminary inquiries indicate that the difference in cost of installation would not be of material import between a suitable press or dryer equipment, while the operating cost would be greatly in favor of the press.

The slight compressibility of water and its extrusion in the restricted space between the plunger and walls of the die, was foreseen; also that a part of the occluded iron would be thus removed. As ferrous sulfate dissolves with contraction of the volume of water, pressure must increase the solubility. It would be interesting to determine the relations between the effect of pressure on the absorbed or adsorbed solute and solvent, but for the present we are obliged to be content with the assurance these experiments have given that it is quite practicable to prepare a cement copper for shipment with an iron content of less than 1 per cent.

Costs

Up to and including April 30, 1925, there has been shipped by the Ohio Copper Co. 17,076,099 lb. of cement copper at a total operating cost of \$656,837.32. The smelting charges during the same period have been \$422,919.22, bringing the total cost of making and marketing the product to \$1,079,756.54. Consequently, on the pound basis, the figures are 3.847 cents for operating; 2.477 cents for smelting charges, and 6.323 cents for making and marketing.

The figure for operating cost includes all labor and materials in leaching, precipitating, mining and exploration, office, laboratory, and salaries at Bingham, Lark, and Salt Lake City. It varies from time to time with production or with the individual items. The cost of the iron per pound of copper produced is approximately 1.25 cents for the metal. More

than half the labor is expended in handling the iron, hence it seems safe to assess half the remaining operating cost to it, bringing the total cost of iron to 2.55 cents, or a little more than 66 per cent. of the total operating cost of making copper under present conditions. Instinctively, the engineer will look here for an opportunity to cut costs. It has been shown that there is possible a small improvement in iron consumption with an increase in the copper content and decrease in the ferric-iron content of the pregnant solution and, doubtless, with the larger mass of scrap that will be required by an increased copper production, there may be a small decrease in the labor item; however, no important change in the present efficient handling of the scrap is foreseen, hence, no important lowering of the cost for iron.

On the other hand, with an increased production of copper and an increased revenue in consequence, it is reasonable to anticipate that a much larger campaign of exploration and development will be inaugurated. All the evidence available, and it is significant in amount and character, is to the effect that there is an enormous territory contiguous to the present caved zone, with a copper content as high, or higher, which can be caved and prepared for leaching. Apparently much of this region can be so prepared economically; experts differ as to the extent to which such operations should be carried. From an engineering point of view, it would be desirable to resume a systematic exploration of the uncaved regions, for it must remain a speculative problem what the life and value of the enterprise may be until a more precise knowledge of the nature of the ore has been obtained, as well as the cost of mining, moving, and crushing it.

LIFE OF THE ENTERPRISE

A visit to the Dederich tunnel, now some 590 ft. into the caved zone, will show that there is much copper sulfate to be removed. It is everywhere apparent that the oxidation of sulfides is continuously in progress, for the temperature is uncomfortably high except at the outlet from the blower; particularly, it will be evident that no leaching has been effected in the part of the caved zone now accessible. Attempts to outline, in diagram, the probable paths of water already applied on the surface but add to the conviction that only a restricted portion of the caved zone has been leached and that the greater part is yet to be so treated. It is evident that the recovery of the copper is to be a gradual process throughout many years. If we accept an estimate of 34,000,000 tons of ore in the caved zone and make a conservative estimate of the average content of copper that may economically be removed by leaching, say 0.3 per cent., and that during the period of removal there will be an average production, annually, of 10,000,000 lb., the life of the operation will be 20 years.

Norden and Crane¹⁰ have estimated the caved zone to contain 251,-218,248 lb. of copper, of which 136,107,463 lb. can be recovered by leaching. Examination of the details of their estimate in the light of our present experience inclines us to the opinion that these engineers were ultra-conservative. They further estimate "proved" territory adjacent to the present caved zone to contain 322,427,696 lb. of which 214,414,418 lb. can be recovered by leaching, although expressing doubt of the economic feasibility of recovering part of this estimated poundage. To resolve these doubts, further exploration work is necessary. In addition, there is a much larger territory of unproved rock, some of which undoubtedly contains sufficient copper to justify leaching, but it is pure speculation at this writing to state quantities. From an engineering point of view, the prospects amply justify an early and systematic exploration of the possible reserves and preparation of new territory for leaching. Other considerations must have their weight. The rapid development of large sources of copper in South America and Africa will undoubtedly have a marked effect on the market, probably in the direction of lower selling values, at least until the world market has been stabilized, and the selling price must be a factor in determining what can reasonably be expended in preparing new leaching territory. Fortunately the proved operating expenses, together with the economies in sight, assure a continued production by the Ohio Copper Co. against any probable competition and for a period to be measured in decades.

DISCUSSION

T. B. BRIGHTON, Salt Lake City, Utah.—There are near Lark 6,000,000 or 7,000,000 tons of tailings from the Ohio Copper concentrators. These tailings contain an average of about 0.4 per cent. copper, partly in an oxidized form. Since leaching of waste rock in the old stopes and fills has proved profitable, the question has been raised as to whether or not a leaching treatment of the tailings would pay. The material in the old ponds is striated and there are lenses of slimes, which are not easily permeable to water, so that any leaching in place in quantity is out of the question. When these claylike slimes are broken up and mixed with the sand tailings, water percolates through the mass quite readily.

At the University of Utah, we have made a few tests to see what recoveries of copper might be expected if the tailings were broken up and leached. The total copper present averages about 8 lb. per ton, but only part of it is water soluble. Long percolation with distilled water dissolves only about 1.5 lb. per ton and a short stirring with three

¹⁰ Private communications; valuation report, January, 1924.

parts water to one part tailings causes only about 0.7 lb. per ton to dissolve.

The only water now available for leaching is that from the precipitating tanks of the company. This flows from the Mascotte tunnel and is distinctly acid in character. Tests made with dilute sulfuric acid, made up 2 lb. of acid per ton of water, showed that approximately 2.7 lb. could be dissolved in 1 to 3 pulp by short stirring. Under the same conditions, the water from the precipitating boxes dissolves 2.8 lb. per ton. Some of this is held up by the water that will not drain from the tailings, so that only about 2.5 lb. can be obtained in the solution for recovery. Repeated percolation over several hours with fresh precipitation box water removes almost half of the total copper present, but not more than the above 2.5 lb. would be in solutions of such concentrations that it could be recovered at a profit by precipitation.

Whether or not the recovery of 2.5 lb. of copper per ton of tailings will pay will depend on the cost of breaking up the bedded material, moving, leaching and dewatering it, and then precipitating the copper. Simple agitation with water does not produce a solution that settles clear quickly so either some type of filtration would be needed or settlers of considerable extent.

A considerable part of the iron in solution is in the ferric state so that precipitation costs on detinned scrap would be above normal. While careful analysis of costs might show a possible profit, the margin, if any, is extremely small. To us, it appears that under present conditions, leaching of the tailings would not prove a profitable undertaking.

In many places on the tailings beds a considerable part of the soluble copper has been carried, by the capillary rise of water, to near the surface. In some spots, the surface is distinctly blue; from such places copper salts are being steadily removed by wind action. So the recoverable copper present in the beds depends on the rate of oxidation of the sulfides and the rate of removal of copper salts by capillary rise and subsequent wind action. Given sufficient time, natural processes will remove a large part of the copper originally present and, when removal is proceeding more rapidly than oxidation of new sulfides, the possible value of the old deposits will drop. So unless copper prices increase or handling methods considerably improve, the tailings ponds are likely to remain undisturbed.

H. C. GOODRICH, Salt Lake City, Utah.—Is there any difference in the amount of iron consumed and copper recovered in these various sections; that is, the first 640 ft. and the second 640 ft.?

A. E. ANDERSON.—Daily analyses are made of the solutions leaving each respective set of sections. The average analyses of these solutions for several months indicate that the consumption of iron per pound of

copper precipitated is about 1 to 1, showing that the consumption of iron throughout the plant is quite uniform and ordinary analytical methods do not detect any greater consumption of iron in any particular set of sections.

H. C. GOODRICH.—Is there any difference in the cost on the tailing and upper ends of the operation?

A. E. ANDERSON.—The labor per pound of copper extracted is practically the same in each section. The unconsumed iron is separated from the copper by washing the precipitated copper through a false bottom into a settling chamber, using a hose placed at regular intervals throughout the plant. The chief iron-consuming constituents of the heading solutions are copper sulfate, ferric sulfate, and some free sulfuric acid. As the ferric iron and the free acid are the only compounds that would produce a high iron consumption per pound of copper precipitated, the lower boxes will contain less of these compounds and consequently the consumption of the iron will theoretically be less. As I have stated, the average analyses of solutions indicate a very uniform consumption of iron throughout the plant. The quantity of ferric iron and acid present in the original heading solution is so small that from a practical standpoint the errors introduced by sampling etc. more than offset this consumption and, therefore, we have the conditions as given. Of course if the ferrous iron were oxidized to ferric during the time the solutions were passing through the sections, one would expect to find the costs of producing copper to be higher in the lower boxes than in the upper but the rate of flow of solutions and the excess quantity of scrap iron prevents the oxidation of the ferrous iron and in very few instances have we found ferric iron in the tailing solutions.

T. P. BILLINGS, Salt Lake City, Utah.—If the iron in the solution containing the copper were increased would the extraction decrease?

A. E. ANDERSON.—The iron in the heading solutions is very constant, therefore I can give no data pertaining to this effect.

T. P. BILLINGS.—We had some experience using solutions from two sources and found that the solution low in iron gave recoveries of the copper around 99.0 per cent., while the solution high in iron gave very low recoveries. I thought that this low recovery was due to the presence of the iron.

F. K. CAMERON.—The fact that all the iron must be reduced before the copper will precipitate will probably account for the low recoveries when using a solution high in iron. The detained iron added in the upper boxes was being consumed by the ferric iron and was not efficiently precipitating the copper; therefore, to obtain the good recoveries it requires more iron which probably, in your case, would mean more boxes, and not having them your recoveries were low.

Leaching Mixed Copper Ores with Ferric Sulfate; Inspiration Copper Co.

BY G. D. VAN ARSDALE, LOS ANGELES, CALIF.

(New York Meeting, February, 1926)

This paper describes a series of experiments leading to the development of a method for leaching the mixed ores of the Inspiration Consolidated Copper Co., containing chalcocite and silicates of copper, by the use of solutions acidified with sulfuric acid and carrying ferric sulfate. Iron is added to the solutions and ferric iron is regenerated electrolytically to a percentage high enough to act as an efficient solvent. The decreased yield is partly compensated for by a higher current density.

AN IMPORTANT problem in modern copper metallurgy, particularly in the Southwest, has been to obtain good recoveries from what are commonly known as *mixed ores*; that is ores in which the copper occurs partly as oxide and partly as sulfide compounds. The dividing line between mixed ores and ores commonly accepted as concentrating is not definite. In other words, much ore now being concentrated carries considerable copper in non-sulfide form, on which recoveries are not so good as on ores carrying less of these constituents. While treatment by concentration may be commercially profitable on ores carrying oxide copper within certain limits, there are large deposits for which the application of concentration could not be considered, and yet which have not been considered amenable to leaching because they carried too much sulfide.

The Inspiration Consolidated Copper Co. has large amounts of such mixed ores, and this paper is an account of the experimental work by which a method was developed for their treatment, and for which a large plant is now being erected by the Inspiration Co. It is not claimed that the method is a general solution of the problem of mixed-ore treatment but it is apparently well adapted for leaching the ores of the Inspiration Co., for which it was designed. The work done has covered preliminary laboratory and test-plant investigation, and a pilot-plant run, extending from March to the middle of December, 1923. Thoroughly consistent and satisfactory results were obtained continuously for more than six months in the pilot plant; and it is believed that the results and probable costs that can be had on a large scale have been definitely proved. The method, however, was designed for local conditions; and while the basic principles are general, there are ores on which it will not work and other ores for which considerable modification may be required.

The definite problem submitted was to devise a method for leaching large tonnages of ore carrying approximately 1.25 per cent. copper, which was known to vary largely in the proportion of sulfide and non-sulfide copper. The main sulfide copper mineral in the ore is chalcocite and the principal non-sulfide chrysocolla. Other copper minerals may occur in small amounts; pyrite also is present but no pyrrhotite. When crushed, the ores leach very well by percolation, and the acid consumption is low. On a scale of operations of, say, 5000 to 7500 tons a day, it was assumed that, in regular working, deliveries of ore could be made carrying total copper between the limits of 1 and 1.3 per cent. As, however, no assurance could be given as to the probable proportion of oxide and sulfide copper in ore which could be maintained day by day, the condition had to be laid down that any method adopted would have to give reasonably good results on any combination of oxide and sulfide within certain limits and inside the above total. On this working scale none of the ore is expected in quantity to be free from sulfide, and in present Inspiration practice an ore of, say, 0.95 per cent. copper as sulfide and 0.25 per cent. as oxide is concentrated; so that for the leaching ore the limits in sulfide and oxide percentages become a minimum and maximum of 0.1 and, say, 0.9 per cent. sulfide and a minimum and maximum of 0.25 and 1.1 per cent. oxide, provided present concentrating practice is followed. While a plant had to be prepared to treat any possible combination, it was believed that the orebody, as a whole, would have an average composition somewhere between, but not at, these limits, as it is a mixed orebody and not one on the edge of being a straight oxide or straight sulfide.

These conditions at once eliminated, for this investigation, consideration of any scheme involving a combination of two methods for the separate recovery of oxide and sulfide respectively. For the problem under consideration, the adoption of such a combination method might mean good metallurgical yields at the expense of uneconomical copper from one or the other of two classes of compounds, in case its percentage in the ore was below the point at which the pounds copper recovered would pay the cost of the individual operation.

In the preliminary survey it was recognized that the probability of eventual cheap electricity and future increasing fuel cost pointed strongly toward electrolytic precipitation. Precipitation with iron, including sponge iron, has attractive features, but for a large installation it requires both cheap fuel and a cheap source of iron; it also means difficulties in the disposal of large amounts of waste liquor and requires comparatively large volumes of fresh water per ton of ore. The desirability of a finished product also favored electrolysis. Precipitation by SO_2 , either from sulfate or chloride liquors, although doubtless feasible and attractive under certain conditions, could in itself be a part of a process for extract-

ing oxide copper only and was, therefore, not considered by the author for this investigation.

CHOICE OF SOLVENT AGENT

Chloride liquors as the solvent agent for copper have some advantages but many practical objections, so sulfate solutions were adopted. As to the actual solution of the copper the oxide portion was not expected to offer any difficulty, from previous work by the Inspiration staff. As it was decided to devise, if possible, a method for extracting both sulfides and oxides together, there remained two alternatives: one, to roast and thereby render the sulfides soluble in dilute acid; the other, to devise a solvent method for extracting sulfide copper direct without roasting. Roasting and leaching are feasible and comparatively simple metallurgically, but this method necessitates a high installation cost for furnaces and a rather delicate control of the roasting operation, with its cost including fuel. It was, therefore, decided to investigate a direct solvent method for copper sulfide; ferric sulfate was the only reagent considered for this purpose.

The literature on this subject was not very encouraging as to the use and regeneration of ferric sulfate. Its experimental use as a solvent is, of course, very old. Its regeneration by air did not appear very promising, and regeneration by electrolysis was stated by all authorities to be possible, when accompanied by plating out of copper, only in very limited percentages; when higher percentages were needed a diaphragm cell was said to be indispensable. Nothing but standard apparatus was wanted, therefore a diaphragm cell was not to be thought of. Fortunately, it was found, notwithstanding these earlier statements, that it was possible to regenerate ferric iron electrolytically in concentration sufficient to act as an efficient solvent of copper sulfide, and at the same time to obtain a reasonable yield, in pounds of copper per kilowatt-hour, in a cell without a diaphragm. Another apparent difficulty was the statement, in the literature, that for compounds of the formula Cu_2S only one half of the copper was readily soluble, that the remaining half required heat and a long time. However true this may be, it was found that a reasonable sulfide extraction percentage could be had in not too long a time on ore crushed sufficiently fine. These facts, namely that an active and efficient ferric sulfate solvent can be regenerated in a non-diaphragm cell by electrolysis with a reasonable yield of copper, and that the solvent thus made, under proper leaching conditions, will give sufficient sulfide extraction, constitute the outstanding features of the method.

CHOICE OF ANODES

In the small-scale electrolytic experiments, both graphite and lead were used as anode materials. The characteristics of graphite are a low

voltage, a high anode efficiency of conversion of ferrous to ferric iron, and durability in the presence of sufficient ferrous iron; but to obtain the minimum voltages with graphite, it is necessary to use agitation and an elevated temperature. Lead anodes gave higher voltages, a lower anode efficiency corresponding to less ferric iron made per unit of copper plated out, and was durable under the conditions of the tests; with lead, agitation and heating were not advantageous. A reasonably high current density, say about 15 amp. per sq. ft., was sufficient to counteract, to a commercial degree, the solvent action at the cathode by the ferric iron produced.

The solution composition adopted was, of course, influenced by the desired leaching action. So far as the electrolysis was concerned, the limits within which the various solution constituents could be varied were found to be about as follows: Copper as sulfate from 2.5 to 3.5 per cent.; total iron from 1.5 to 2.5 per cent.; ferric iron up to 1.0 per cent. or somewhat higher; free acid from 3.5 to, say, a maximum of 7.5 per cent. With the minimum or more of copper, that is the amount necessary to obtain good reguline copper, no important effect was observed on increasing this percentage. Reduction of voltage is had by the presence of sufficient ferrous iron and no harmful effect on electrolysis is brought about by increase of this constituent; ferric iron in considerable amounts increases voltage; increasing percentages of free acid reduce voltage.

With either lead or graphite anodes, the cathode and anode efficiencies do not necessarily follow the same curves, and it is possible in several ways to establish conditions by which these efficiencies can be varied independently where this effect is desirable. This means that the production of ferric iron does not necessarily correspond to the amount of copper plated out. There is considerable advantage in being able to vary the amount of ferric iron relative to the copper plated out, for in this way the ferric-iron balance may be preserved notwithstanding considerable variations in the proportions of oxide and sulfide copper in the ores being leached.

A diaphragm is not needed to obtain reasonable yields in the presence of ferric iron, up to about 1 per cent. or even a little more. By a reasonable yield is meant a cathode efficiency of, say, not less than 60 per cent. and about $\frac{2}{3}$ lb. copper per kilowatt-hour. Alumina is not harmful; and when present in the electrolyte in sufficient amounts has a beneficial effect on cathode efficiency in the presence of ferric iron. Up to about 0.5 per cent. or more of copper can be plated out from solution, and the copper is of good physical character and of sufficient purity chemically to meet standard specifications.

SIZE OF ORE

In the preliminary survey on leaching, it was felt that a system should be devised that would involve percolation although leaching by agitation

and counter-current washing has attractive features. With a finely crushed ore, the time of contact of the acid solvent, it could be expected, would be reduced to a matter of hours with agitation, as against days by percolation with probably increased extraction. However, there are disadvantages in this method of leaching. Fine crushing costs more per ton, and the extra extraction obtainable may not be sufficient to balance this extra cost. The amount of fresh water needed per ton of ore is much larger and the volume of the various washes much greater than by percolation; for in percolation an ore charge can be drained to contain not more than from 10 to 15 per cent. moisture, while in agitation of finely crushed ore, settling can hardly be done to a less ratio than 1:1 of solution to ore. This means about ten times the volume of fresh water and of the several washes necessary for agitation treatment as compared with percolation. For a large plant, this large volume of water is an important consideration. Also dry crushing to a size fine enough to agitate is not an attractive proposition. In addition acid-proof agitators have not been built and operated in the large sizes that would be required; while no doubt they could be developed, one of the requirements of the method sought was that it should require nothing but standard and proved apparatus. Therefore, unless the test results showed that agitation had to be adopted, it was not considered desirable for the problem under consideration.

The tentative conclusions, made as a result of laboratory-scale leaching tests on representative ore, were as follows: All forms of oxide copper present in the ore were readily and completely soluble in the solutions used. Copper in the sulfide form present (chalcocite) gave 80 to 85 per cent. extraction when treated warm (about 125° F.) with the solutions used and about 75 per cent. extraction to the same solutions cold, under parallel conditions. The degree of crushing was of little importance, with regard to oxide extraction, but was of primary importance in respect to sulfide extraction; that is, it was proved necessary to reduce the ore to a given fineness to obtain satisfactory sulfide extraction in a reasonable time with either warm or cold solutions. The reason for this was not only the different chemical reactions but also the quite different way in which the two minerals occur in the ore. The copper silicate is usually along fracture planes etc. of appreciable size and thus is much more accessible to the action of the solutions than the chalcocite; this was afterwards demonstrated by microscopic examination of ore leached on a large scale. It was also shown that below a percentage of, say, about 0.4 per cent. Fe⁺⁺⁺, the solvent action of ferric iron becomes feeble; while at 0.75 to 1 per cent. or above, ferric iron is an active solvent. Therefore, while it was theoretically possible and desirable, from the electrolytic standpoint, to obtain a complete reduction of ferric iron during the leaching, practically the minimum ferric iron in the solution from the ore would be about 0.5 per

cent. and preferably higher; and from the leaching standpoint the higher the better. The Inspiration ore is markedly different from that of the New Cornelia Co. in that the amount of iron dissolved per cycle is small; it is, in fact, less than the amount that would normally be carried from the system by the last wash waters when leaching with a solution carrying about 2.5 per cent. total iron. This means that no discard is necessary to prevent accumulation of iron; also that it is possible to standardize the solutions at any given percentage of total iron, provided losses of iron are made up.

These tentative conclusions were thoroughly investigated in a small test plant, when the results apparently showed that tailings containing not more than about 0.2 per cent. copper could be expected. A tentative flow sheet was then adopted and recommendations made for a large-scale test in a pilot plant. No substantial changes were made in this flow sheet as the result of the larger scale work, and the average recovery made in the pilot plant checked closely that predicted from the small-scale work.

PILOT-PLANT OPERATIONS AND RESULTS

The Inspiration company had a well-designed and very flexible pilot test plant and a competent staff experienced in leaching and electrolytic work, so it was decided to have further work done in the pilot plant, under the charge of the local staff, with the author as consultant. A few minor changes only were needed to adapt the pilot plant for the new method, and after these were made operations were started about March 1, 1923.

The first month was spent leaching high-grade ore for the purpose of making up the solutions. For about a month or six weeks afterwards, ore furnished by the mine carried higher percentages of sulfide than would be expected in regular operations on a large scale. During this period, also, conditions were not adjusted to furnish sufficiently strong ferric iron for leaching. When this was accomplished, decided improvement was shown. A little later, beginning about May 1, ore more nearly representative in grade and sulfide percentage was furnished and results were satisfactory. During July, seven lots were crushed finer, with the idea of possibly bettering the sulfide extraction, and later some tests were made on shortening the leaching cycle. Following this, uniform operating conditions were established, as nearly as possible, and operation was continued for a sufficient time to make as sure as possible on this scale of all factors. Altogether, about six months of consistent and satisfactory results were had, which was considered a sufficient demonstration of the method.

The details of the leaching operations and results for these periods, with some comments on the results as obtained, are as follows:

SERIES 1

Preliminary period for solution make-up.

Conditions—finely crushed high-oxide ore.

Average analysis of ore: Total copper, 2.16 per cent.; soluble copper, 1.94 per cent.; sulfide copper, 0.22 per cent.

Lot No.	Heads			Tails				Extraction		
	Total Cop- per, Per Cent.	Sol- uble Cop- per, Per Cent.	Sulfide Cop- per, Per Cent.	Total Cop- per, Per Cent.	Sol- uble Cop- per, Per Cent.	Sulfide Cop- per, Per Cent.	H ₂ O Sol- uble Cop- per, Per Cent.	Total, Per Cent.	Sol- uble, Per Cent.	Sulfide, Per Cent.
1	2.20	2.07	0.13	0.40	0.30	0.10	0.16	81.8	85.5	23.1
2	2.44	2.28	0.16	0.46	0.36	0.10	0.12	81.2	84.3	37.5
3	3.44	3.34	0.10	1.49	1.39	0.10	0.14	56.7	58.4	
4	3.0	2.87	0.13	1.93	1.83	0.10	0.32	35.7	36.3	23.1
5	2.87	2.72	0.15	2.08	1.97	0.11	0.35	27.5	27.6	26.6
6	1.80	1.23	0.57	1.22	0.72	0.50	0.24	32.2	41.5	12.3
7	1.84	1.23	0.61	1.80	1.20	0.60	0.24			
8	1.46	1.22	0.24	0.69	0.45	0.24	0.10	52.7	63.1	
9	1.30	1.21	0.09	0.50	0.43	0.07	0.09	61.5	64.4	22.2
10	1.30	1.25	0.08	0.50	0.46	0.04	0.08	62.4	63.1	50.0
Average.....	2.16	1.94	0.22	1.10	0.91	0.19	0.18	49.1	52.4	19.4

The results of this first series were very poor, and unexplainedly so. The leaching agent during most of the time was sulfuric acid, containing copper sulfate and ferrous sulfate, with but little ferric iron until the electrolysis was started; therefore little, if any, sulfide extraction was to be expected but the oxide extraction also was low. The first lot out was reasonably good, but from this time up to lot 7 extractions were increasingly bad; lot 7 gave practically no extraction. It is difficult to see how an ore carrying oxide copper could have been exposed to the action of an acid leach for ten days and no copper be removed. It may be possible that some unobserved leaching condition, possibly due to a green crew, was responsible for these figures. The ore was finely crushed and channeling occurred, resulting in poor percolation and washing, but the conditions were uniform, so far as the author is aware, in the several tanks and should not therefore have shown uniformly decreasing extraction to such a degree. Precipitation of iron salts, carrying some copper, was observed on the ore in some places in the tanks, probably due to insufficient acidity, but this could hardly have been in sufficient amount to account for the results.

Lot 8 was the first to have a complete treatment with electrolyte, and some improvement was noted. It was decided at this time to try coarser crushing, so a 3-mesh screen was installed and the ore crushed through

this size. The acid strength also was raised high enough to prevent precipitation of basic compounds from solution onto the ore. The following results were obtained on this series:

SERIES 2

High-grade mixed ore.

Conditions—low ferric iron, 3-mesh crushing.

Average analysis of ore: Total copper, 1.81 per cent.; soluble copper, 0.82 per cent.; sulfide copper, 0.99 per cent.

Lot No.	Heads			Tails				Extraction		
	Total Cop-per, Per Cent.	Sol-uble Cop-per, Per Cent.	Sulfide Cop-per, Per Cent.	Total Cop-per, Per Cent.	Sol-uble Cop-per, Per Cent.	Sulfide Cop-per, Per Cent.	H ₂ O Soluble Cop-per, Per Cent.	Total, Per Cent.	Sol-uble, Per Cent.	Sulfide, Per Cent.
11	1.58	0.87	0.71	0.58	0.13	0.45	0.08	63.3	85.1	33.6
12	1.11	0.79	0.32	0.20	0.04	0.16	0.02	82.0	95.0	50.0
13	1.15	0.90	0.25	0.31	0.17	0.14	0.05	73.0	81.1	44.0
14	1.83	0.91	0.92	0.81	0.18	0.63	0.03	56.3	80.2	31.5
15	2.06	0.93	1.13	1.18	0.34	0.84	0.08	42.7	63.4	25.7
16	2.21	0.79	1.42	0.72	0.08	0.64	0.03	67.5	89.9	54.9
17	2.22	0.92	1.30	0.99	0.16	0.83	0.03	55.4	82.6	36.2
18	2.08	0.61	1.47	0.99	0.07	0.92	0.02	52.4	88.5	37.4
19	2.01	0.92	1.19	0.97	0.16	0.81	0.04	51.8	80.5	31.9
20	1.57	0.77	0.88	0.49	0.04	0.45	0.02	68.8	94.8	43.8
21	1.88	0.94	0.94	0.65	0.17	0.48	0.05	65.4	81.9	48.9
22	1.65	0.77	0.88	0.77	0.16	0.61	0.06	53.3	79.2	30.7
23	2.22	0.76	1.26	0.80	0.14	0.66	0.07	64.0	85.4	47.6
Average.....	1.81	0.82	0.99	0.72	0.14	0.58	0.04	61.2	83.6	39.7

The results during this period were improved, but were far from satisfactory. The soluble copper extraction was fairly good and the size of the ore, as now crushed, gave good percolation and fairly good washing. The average percentage of sulfide extraction, and consequently the total extraction were still very low, although occasionally fairly good sulfide extractions were obtained. Toward the end of this series, it was found that through a misunderstanding, the wash waters, which were regularly advanced, were being added to the solution for leaching, instead of to the solutions for electrolysis, where they obviously belonged. When this procedure was changed, the increased ferric iron in the leach liquor at once gave improved leaching extraction from the sulfides. Also, at this time, the ferric iron in the solution from the tank house was allowed to increase; this change, as could be expected, gave improved sulfide extractions. These improved results became increasingly apparent at the beginning of the next series, the results from which were as follows:

SERIES 3

High-grade mixed ore.

Conditions—High ferric iron.

Average analysis of ore: Total copper, 1.82 per cent.; soluble copper, 0.61 per cent.; sulfide copper, 1.21 per cent.

Lot. No.	Heads			Tails				Extraction		
	Total Cop- per, Per Cent.	Sol- uble Cop- per, Per Cent.	Sulfide Cop- per, Per Cent.	Total Cop- per, Per Cent.	Sol- uble Cop- per, Per Cent.	Sulfide Cop- per, Per Cent.	H ₂ O Sol- uble, Per Cent.	Total, Per Cent.	Sol- uble, Per Cent.	Sul- fide, Per Cent.
24	2.17	0.33	1.34	0.65	0.10	0.55	0.08	70.1	87.9	58.9
25	2.16	0.89	1.27	0.67	0.10	0.57	0.06	69.0	88.8	55.1
26	1.67	0.52	1.15	0.43	0.05	0.38	0.04	74.3	90.4	56.9
27	1.70	0.61	1.09	0.47	0.03	0.44	0.02	72.4	95.1	59.6
28	1.72	0.75	0.97	0.57	0.12	0.45	0.09	66.9	84.0	53.6
29	1.51	0.59	0.92	0.66	0.21	0.45	0.12	56.3	64.4	51.1
Average.....	1.82	0.61	1.21	0.57	0.12	0.47	0.06	68.1	85.1	57.5

The results from this series were quite encouraging. The oxide extraction was fairly good, although the washing efficiency had gone back somewhat, compared with the last series. The average sulfide extraction, however, was decidedly improved.

While the improvement was noted and while the feed was still high in total and sulfide copper, not much enthusiasm could be expected over tailings averaging 0.57 per cent. total copper. The method and flow sheet had been designed for an orebody averaging about 1.25 per cent. total copper, and some modification, for which experimental data were not at hand, would have to be made to leach efficiently ore with much higher sulfide than planned. As most of the lots received had not been representative, arrangements were made to hold the ore deliveries to the test plant as closely as possible to the general average of the ore as a whole, although on account of the uncertainty as to the probable percentage of oxides, no restrictions were imposed as to the relative amounts of sulfides and oxides. In either a small or large way it is difficult to mine ore conforming to any restrictions. For the purposes of the tests, it was necessary to draw oxide and sulfide from separate locations and mix these to the required grade of total copper before delivery to the test plant, and credit and thanks are due to the mining department for the trouble it took to secure representative ore for these tests in the midst of, and interfering with its normal operations. The following results were obtained from the next series of tests:

SERIES 4

Representative ore.

Conditions—high ferric iron, total leaching cycle 14 days.

Average analysis of ore: Total copper, 1.38 per cent.; soluble copper, 0.82 per cent.; sulfide copper, 0.55 per cent.

Lot No.	Heads			Tails				Extraction		
	Total Cop- per, Per Cent.	Sol- uble Cop- per, Per Cent.	Sulfide Cop- per, Per Cent.	Total Cop- per, Per Cent.	Sol- uble, Cop- per, Per Cent.	Sulfide Cop- per, Per Cent.	H ₂ O Sol- uble Cop- per, Per Cent.	Total, Per Cent.	Sol- uble, Per Cent.	Sul- fide, Per Cent.
30	1.13	0.69	0.44	0.24	0.08	0.16	0.07	78.8	88.4	63.7
31	1.31	0.75	0.56	0.28	0.07	0.21	0.05	78.7	90.7	62.5
32	1.74	0.84	0.90	0.30	0.07	0.23	0.06	82.8	91.7	74.5
33	1.21	0.61	0.60	0.25	0.03	0.22	0.03	72.3	95.1	63.3
34	1.39	0.77	0.62	0.27	0.05	0.22	0.05	80.6	93.5	64.5
35	1.19	0.64	0.55	0.24	0.05	0.21	0.04	79.8	92.2	61.8
36*	1.54	0.79	0.75	0.58	0.22	0.36	0.09	62.3	72.2	52.0
37	1.34	0.67	0.67	0.40	0.04	0.36	0.04	70.1	94.0	46.3
38	1.48	0.78	0.70	0.24	0.02	0.22	0.02	83.8	97.5	68.6
39	1.21	0.71	0.50	0.25	0.01	0.24	0.01	79.3	98.6	52.0
40	1.22	0.69	0.53	0.09	0.01	0.08	0.01	92.6	98.6	84.0
41	1.16	0.74	0.42	0.15	0.05	0.10	0.05	87.1	93.2	76.2
42	1.12	0.75	0.37	0.11	0.01	0.10	0.01	90.2	98.7	73.6
43*	1.17	0.62	0.55	0.53	0.17	0.31	0.05	54.7	72.5	43.6
44	1.16	0.67	0.49	0.14	0.02	0.12	0.02	87.9	97.0	75.5
45	1.29	0.65	0.64	0.17	0.01	0.16	0.01	86.0	98.4	71.8
46	1.21	0.89	0.32	0.17	0.02	0.15	0.02	85.9	97.7	53.1
47	1.19	0.90	0.29	0.11	0.01	0.10	0.01	90.7	98.8	65.5
48	1.23	0.98	0.25	0.13	0.02	0.11	0.01	89.4	97.9	56.0
49	1.15	0.97	0.18	0.11	0.02	0.09	0.02	90.4	97.9	50.0
50*	1.35	1.04	0.31	0.22	0.09	0.13	0.03	83.7	91.4	58.1
51	1.48	1.13	0.35	0.11	0.02	0.09	0.02	92.6	98.3	74.3
52	1.57	0.98	0.58	0.15	0.01	0.14	0.01	90.7	99.0	76.6
53	1.55	0.99	0.56	0.24	0.01	0.23	0.01	84.5	99.0	59.0
54	1.42	0.84	0.58	0.16	0.01	0.15	0.01	88.9	98.9	74.2
55	1.64	0.96	0.68	0.20	Tr	0.20	Tr.	87.8	99.9	70.2
56	1.77	0.99	0.78	0.77	0.01	0.26	0.01	84.7	99.0	66.7
57*	1.68	1.01	0.67	0.41	0.12	0.29	0.07	75.6	88.1	56.7
58	1.79	1.06	0.73	0.20	0.01	0.19	0.01	88.9	99.1	74.0
59	1.47	0.85	0.62	0.14	0.14	90.4	99.9	77.0
60	1.73	0.96	0.77	0.17	0.17	90.1	99.9	78.0
61	1.56	0.94	0.62	0.16	0.16	89.7	99.9	74.0
Average.....	1.38	0.83	0.55	0.19	0.03	0.16	0.02	85.5	96.8	67.3

* Omitted from averages on account of trouble with No. 1 leaching tank.

The average results from this series were entirely satisfactory, the average tailings showing 0.19 per cent. total copper, 0.03 per cent. soluble

copper, 0.17 per cent. sulfide copper, and 0.02 per cent. water soluble copper, from a feed averaging 1.38 per cent. total copper. The extraction of the soluble copper was high, a number of lots showing over 99 per cent., a result somewhat higher than that had in previous work on similar ore with acid leaching.

The washing efficiency in this series averaged very well; in some cases a nearly complete removal of the dissolved copper was obtained. This was probably due largely to a washing system applied during most of the runs of this series. This method had been tested in previous work by the company, without arriving at definite conclusions, but as it had several possible advantages for the new leaching method, a decision was made to test it further. The fourth series had used the ordinary washing methods, and about eight washes of unit volume each had left in the tailings from $\frac{3}{4}$ to $1\frac{1}{4}$ lb. or more of recoverable copper. Since using the new method, it was demonstrated that less than $\frac{1}{4}$ lb. dissolved copper left in the tailings is easily possible. The method, called a circulating wash, is simple; it consists in first applying the usual regular unit volume washes, which are advanced in the usual manner. After applying these and draining, an additional wash is put on, taken off, passed through a scrap-iron launder or other cementation device, and again circulated through the ore and the launder, until satisfactory dissolved copper extraction is had, which can be taken to be somewhat above the point at which the copper recovered balances the pumping and other washing costs. As these are low, a high soluble recovery is possible by the method without the necessity, as in the ordinary system, of carrying too large a number of stock washes with consequent large storage capacity. This special wash may be applied after any particular number of regular washes, which are advanced into the system, therefore the total amount of copper produced as cement need not be any considerable percentage of the total production. Any cement copper produced can, of course, be dissolved in the main leach liquor and finally appear as cathodes. The method has the advantage also, for this particular leaching process, of forming a stock of dissolved iron from which any required amount may be drawn for the purpose of making up main solution losses in this element. In this way the main solution can be kept at any desired percentage of total iron, which is desirable in respect to the control of ferric-iron balance.

A few lots were crushed to pass a $\frac{1}{4}$ -in. opening, instead of the 3-mesh, and the following results were obtained:

SERIES 5

Representative ore.

Conditions—Same as series 4, with finer crushing.

Average analysis of ore: Total copper, 1.46 per cent.; soluble copper, 0.85 per cent.; sulfide copper, 0.61 per cent.

Lot	Heads			Tails				Extraction		
	Total Copper, Per Cent.	Sol- uble, Copper, Per Cent.	Sulfide Copper, Per Cent.	Total Copper, Per Cent.	Sol- uble Copper, Per Cent.	Sulfide Copper, Per Cent.	H ₂ O Sol- uble Copper, Per Cent.	Total, Per Cent.	Sol- uble, Per Cent.	Sul- fide, Per Cent.
61	1.54	0.94	0.62	0.16	tr.	0.16	tr.	89.8	99.9	74.2
62	1.82	1.11	0.71	0.24	0.01	0.23	0.01	86.9	99.2	67.6
63	1.33	0.89	0.44	0.16	0.03	0.13	0.03	88.0	96.7	70.5
64	1.39	0.91	0.48	0.18	0.01	0.17	0.01	87.1	98.9	64.6
65	1.55	0.90	0.65	0.09	tr.	0.09	tr.	94.2	99.9	86.2
66	1.41	0.74	0.67	0.16	tr.	0.16	tr.	88.7	99.9	76.1
67	1.27	0.65	0.62	0.14	tr.	0.14	tr.	89.0	99.9	77.5
68	1.38	0.71	0.67	0.15	tr.	0.15	tr.	89.1	99.9	77.6
Average	1.46	0.85	0.61	0.16	0.006	0.154	0.006	89.1	99.3	74.3

The average results from this series, although including the high record for sulfide and total extraction, were nearly the same as the averages for the series preceding and following; the conclusion was therefore reached that, for the ore as furnished, crushing to finer than 3-mesh was not necessary. This conclusion seems warranted from the results of this series, but it is at variance with some data from screen analyses.

Table 1 shows the leaching averages covering the entire period of the test-up to the shutdown in December.

During September, the policy was adopted of drawing lots of ore from various parts of the orebody, with no restrictions as to grade or proportion of oxide and sulfide. This was, of course, desirable from the point of view of sampling the deposit; but resulted in an erratic feed and it is surprising that under these difficult conditions good results were obtained. For any metallurgical method, a regular and uniform feed is an important factor in securing good results, and this month's work may be considered to have demonstrated the flexibility of the method in this respect. With a uniform supply of any of the different grades and kinds of ores treated, it is quite likely that somewhat better results could have been had.

TABLE 1.—*Extraction Data, 1923*

	Feed, Per Cent. Copper			Tailing, Per Cent. Copper				Extraction, Per Cent.		
	Total	Soluble	Sulfide	Total	Soluble	Sulfide	Water Soluble	Total	Soluble	Sulfide
Jan.....										
Feb.....										
March.....	2.030	1.750	0.280	0.990	0.770	0.220	0.160	50.90	56.00	21.50
April.....	1.905	0.811	1.094	0.727	0.130	0.597	0.045	61.90	83.97	45.40
May.....	1.340	0.710	0.630	0.322	0.079	0.243	0.050	76.00	88.87	61.40
June.....	1.430	0.940	0.490	0.184	0.024	0.160	0.016	87.13	97.45	67.35
Average.....	1.653	1.012	0.641	0.530	0.221	0.309	0.063	67.90	78.20	51.60
July.....	1.424	0.830	0.594	0.150	0.004	0.146	0.004	89.42	99.52	75.32
August.....	1.335	0.468	0.867	0.248	0.226	0.022	0.026	81.40	94.40	74.40
Sept.....	1.820	0.910	0.910	0.234	0.008	0.226	0.006	87.15	99.12	75.16
Oct.....	1.306	0.839	0.467	0.181	0.005	0.176	tr.	81.15	99.40	62.30
Nov.....	1.259	0.552	0.707	0.163	0.009	0.154	0.009	87.05	98.37	78.22
Dec.....	1.198	0.461	0.737	0.264	0.022	0.242	0.022	77.96	95.12	67.23
Average....	1.403	0.692	0.711	0.199	0.012	0.187	0.011	85.80	98.30	73.70
Year average	1.504	0.821	0.683	0.333	0.096	0.237	0.032	77.90	88.30	65.30

Table 2 represents monthly average results from the operation of the tank-room part of the 35-ton test plant:

TABLE 2.—*General Tank-house Data*

Month	Current Density	Cathode Eff., Per Cent.	Anode Eff., Per Cent.	Lb. Cu. per Kw.-hr., D.C.	Entering Temp., Degrees C.	Departing Temp., Degrees C.	Atmos. Temp., Degrees C.
Jan.....							
Feb.....							
March.....	15.1	54.2	47.0	0.696	53.8	43.5	12.4
April.....	14.5	54.3	82.1	0.670	47.7	44.9	17.2
May.....	14.5	56.9	43.2	0.605	24.0	28.0	25.0
June.....	14.7	63.6	38.0	0.666	26.0	30.0	28.0
Average.....	14.65	57.2	51.8	0.667	30.1	35.7	21.8
July.....	14.8	64.6	47.3	0.698	29.0	35.0	29.0
Aug.....	14.7	67.5	70.2	0.784	38.0	41.0	26.0
Sept.....	14.5	66.9	55.3	0.750	28.0	33.0	23.0
Oct.....	14.5	62.7	34.4	0.660	22.0	32.0	17.0
Nov.....	15.0	68.5	65.4	0.744	28.0	34.0	11.0
Dec.....	24.6	58.5	83.1	0.559	43.0	42.0	6.0
Average.....	15.28	65.4	55.2	0.715	30.5	35.8	20.2
Year average.....	15.00	62.1	53.9	0.695	30.4	35.8	20.8

At the start of operations, the solutions in the tank house during electrolysis were agitated by air and heated by steam in a separate tank before entering. These two steps are of benefit when graphite anodes are used but not with lead, and were discontinued. A number of changes in solution composition, operating conditions, etc. were made before uniform conditions were adopted. Generally speaking, there was little difference between the tank-room operating conditions during these tests, and those of previous work during acid leaching. The main difference in results was the lower yield in pounds copper per kilowatt-hour, which averaged over the whole work about 0.7 lb. as compared with about 1.1 lb. for the electrolytes in which ferric iron was present in only small amounts. There appeared to be little difference in the behavior of the lead anodes used, their warping, etc. as compared with previous work. The cathodes produced were of good physical quality, and little trouble was caused by sprouting. It seems probable that an average yield of about 0.7 lb. per kw.-hr. can be expected. The cathode efficiency falls off with increasing weight. As they grow thicker the cathodes become rougher and expose more surface to chemical corrosion, which is probably the reason for the observed lessened efficiency. Tests made at higher current densities than 15 amp. per sq. ft. did not indicate that the higher current densities would be desirable. It does not seem likely that contamination of tank-room atmosphere, due to gas from the anodes, will be sufficient to cause trouble.

DESCRIPTION OF PILOT PLANT

The plant used for the work described was operated during previous large-scale tests by the Inspiration Co.; for the present work, very little change was required. As a matter of fact, there is practically little difference in design for a plant operating by this method and one using straight acid leaching; it will therefore not be necessary to describe the pilot plant in detail.

The nominal capacity was about 35 tons per day. The ore, after fine crushing, was delivered to a storage bin located at the end and above the leaching-plant top level. From this bin, the ore was drawn into a small car, running on a track along the top of the tanks, into which it was discharged from the car through a V-shaped arrangement, which distributed it as uniformly as possible. The seven rectangular leaching tanks were made of concrete and lined with lead throughout. Pumping and circulation arrangements provided for either upward or downward circulation; also for circulating a part of the total flow through an individual tank and advancing the remainder to the next tank. During the leaching, percolation was upward, with a maximum flow of 0.25 gal. per ton per minute. The total leaching cycle was about 14 days;¹ of this about one day each is required for loading and unloading, and about three days

washing time, leaving about nine days as acid contact time. After washing, the tanks were discharged by hand through a door at the lower part of the front side of each tank on to a belt conveyor, from the end of which a sample was taken during the unloading.

In the tank room, except for a short period, lead anodes were used, which were taken out and straightened at intervals. Daily weighings of the copper plated out were recorded. Tests showed that starting sheets could be made from the solutions used, although during the work these were supplied through the courtesy of the New Cornelia Co. Arrangements were made for warming the solutions, which was done for a time toward the close of the tests. After a few days experience with cutting off of cathodes at the solution level, a solid loop was used, painted at the solution level with P & B paint; no cathodes dropped after this was done.

The circulating wash was passed through a launder filled with scrap iron, after which it was pumped back on to the ore or to storage; the launder was cleaned up at intervals. Small-scale tests showed the ready solubility of the cement copper produced, which, together with the cathodes, were shipped to the International smelter.

Sufficient samples were taken for plant control; on these the standard assay methods were used. The accuracy of these and of the control was demonstrated by the copper balance made at the close of operations.

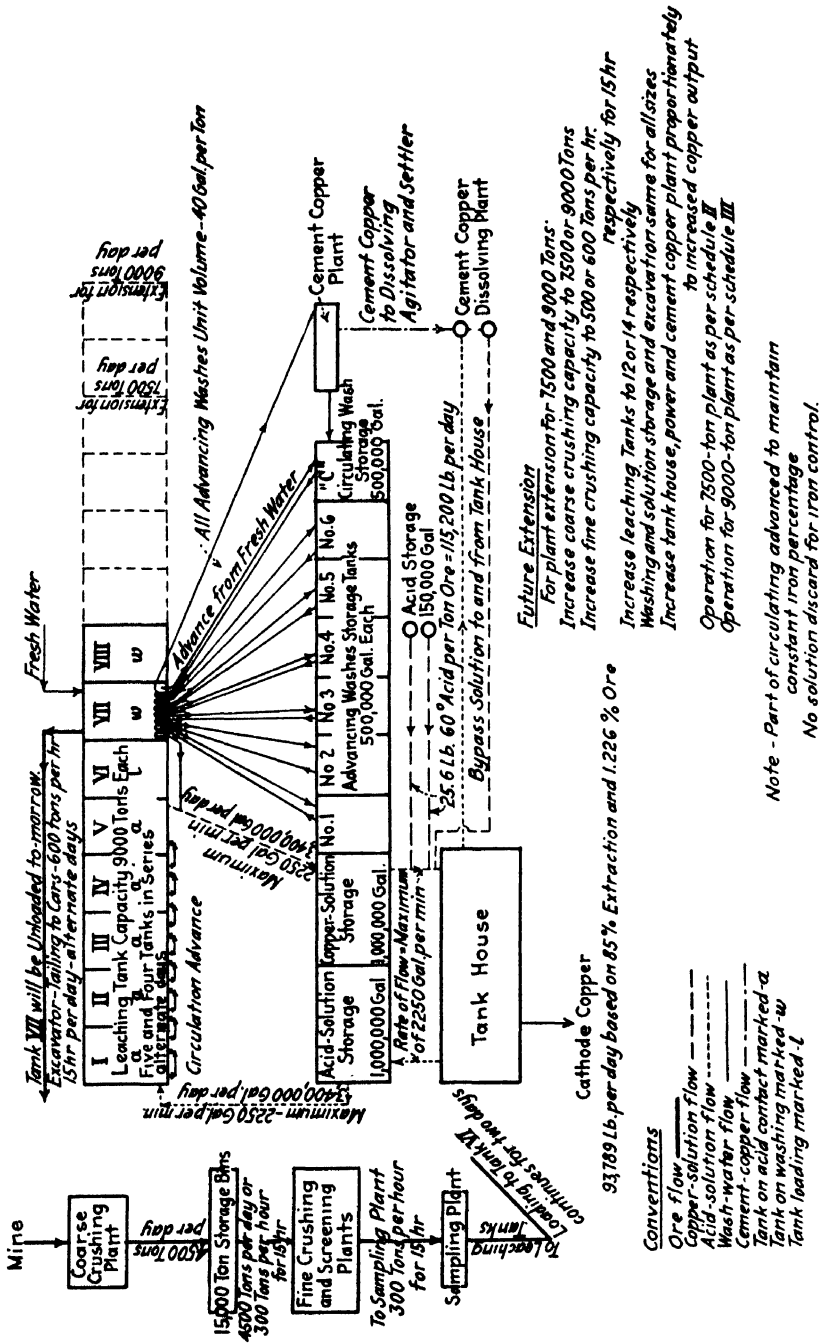
COPPER BALANCE MARCH TO DECEMBER, 1923, INCLUSIVE

	POUNDS
Copper in ore received and treated	152,378
Electrolytic copper produced, 100 per cent.....	93,729
Cement copper produced, 100 per cent.....	18,145
Total produced	111,874
Copper discarded in tailing.....	33,809
Copper inventory, reserved for experimental purposes.....	5,161
Total accounted for.....	150,844
Per cent. of total accounted for.....	99

The figures for extra new acid needed during the entire test period remained very consistently at close to 20 lb. actual H_2SO_4 per ton of ore treated.

To summarize the results obtained, a diagrammatic flow sheet is shown, Fig. 1. This is meant to be illustrative only, and details of the large plant will vary from it. As shown, it consists of the following steps:

1. Coarse crushing to $1\frac{1}{2}$ in.
2. Fine crushing to pass 3-mesh.
3. Conveying without intermediate storage, to leaching tanks.



4. Leaching, consisting of maximum contact of 9 days with acid ferric-sulfate leach liquor, applied counter-currently; that is, strongest solution to oldest ore, the leaching tanks being in series, and the solution taken to tank house after passing through the newest ore.

5. Washing, taking 3 days, and consisting of application of six washes, each of unit volume and advanced after each cycle, the strongest joining the copper solution to the tank house, and followed by a circulating wash pumped through the ore until sufficient soluble copper is removed. A portion equivalent to unit volume of this circulating wash is advanced to the sixth wash storage, being replaced by fresh water of the same volume, which may be passed over the leached ore, to recover iron as needed.

6. Discharge of tailings.

7. Electrolysis.

8. Solution of cement copper from circulating wash in acid solution from tank house, bypassed and returned with main solution feed to tank house.

ACKNOWLEDGMENTS

In conclusion, the writer wishes to express appreciation and thanks to Dr. L. D. Ricketts, President, and Mr. T. H. O'Brien, General Manager, of the Inspiration Cons. Copper Co., for the opportunity of working on the problem; to Mr. Harley A. Sill, of the firm of Sill & Sill, Los Angeles, Calif., for efficient help during the preliminary test period; to Mr. MacDonald, and Mr. Stoddard of the Inspiration Mining Dept. for their coöperation; and to Mr. H. W. Aldrich, Asst. Gen. Supt. in charge of leaching tests, and Mr. W. G. Scott under his direction, together with the other members of the local leaching staff for their ability and coöperation in securing the results obtained. It has been a real pleasure to work with an organization whose spirit throughout has been coöperation and the wish to obtain facts, and particularly gratifying to one coming from outside the regular company organization with a method competitive with successful preceding work along the same lines.

DISCUSSION

H. A. TOBELMANN, Salt Lake City, Utah (written discussion).—With the possible exception of the differences in ferric sulfate reduction and current density, the process described is similar to that developed and successfully used by the New Cornelia Copper Co., in treating some 13,000,000 tons of oxidized ore.

The first of these exceptions, the reduction of the ferric sulfate, is due to the difference in the composition of the ore. Ferric sulfate in contact with soluble sulfides is reduced to ferrous sulfate, doing

away with the necessity of sulfur dioxide. While both processes use both ferric sulfate and sulfuric acid as the lixiviant, the quantity of sulfide present in the average leaching ore at Ajo was not sufficient to reduce the ferric sulfate to an appreciable extent and sulfur dioxide was necessary. The predominating sulfide at Ajo is chalcopyrite while at Inspiration it is chalcocite.

The oxidized portion of the Ajo orebody contained at all times appreciable quantities of sulfide, which increased with depth. That this sulfide would affect the percentage extraction was known, and the problem arising from its presence was frequently discussed. It was known that the lixiviant would quite readily dissolve chalcocite, and that it would have but little solvent action on the bornite and practically none on the chalcopyrite. From the beginning of operations, including the experimental work, the insoluble, oxide and sulfide portions of the ore were determined on both the heads and the tailings. The determination of the insoluble portion of the copper indicated the percentage existing as sulfide because no insoluble oxidized copper minerals were present. From a little less than 3 per cent. of the total copper in 1917, this insoluble portion increased to nearly 15 per cent. in 1924. The results on the yearly composite samples on the heads and tailings for 1920 are as follows:

DISTRIBUTION OF TOTAL, OXIDE, SULFIDE AND SOLUBLE COPPER IN THE HEADS AND TAILS FOR DIFFERENT MESH, AND THE EXTRACTION OF THESE SIZES FOR 1920, NEW CORNELIA COPPER CO.

Heads, Percentage Copper (By Difference)

Mesh	Per Cent.	Total	Oxide	Sulfide	Soluble	Insoluble (By Difference)
On 3	26.6	1.37	1.23	0.14	1.28	0.09
4	18.6	1.33	1.18	0.15	1.23	0.10
6	13	1.39	1.25	0.14	1.30	0.09
8	9.1	1.46	0.30	0.16	1.34	0.12
10	6.4	1.55	1.39	0.16	1.43	0.12
14	5.0	1.62	1.46	0.16	1.49	0.13
20	3.1	1.75	1.57	0.18	1.62	0.13
20	18.0	2.06	1.82	0.24	1.83	0.18
	Computed: (1) 100.0	1.534	1.368	0.167	1.416	0.118
Arithmetical						
(2) Average of all assays.		1.525	1.362	0.163	1.396	0.123
(3) Assay of composite sample.....		1.500	1.340	0.160	1.390	0.110

Tailings, Percentage Copper (By Difference)

Mesh	Per Cent.	Total	Oxide	Sulfide	Soluble	Insoluble (By Difference)
On 3	25.8	0.47	0.35	0.12	0.37	0.10
4	20.1	0.32	0.21	0.10	0.23	0.09
6	12.5	0.25	0.14	0.11	0.15	0.10
8	8.7	0.21	0.10	0.10	0.11	0.10
10	7.2	0.21	0.09	0.12	0.10	0.11
14	4.8	0.21	0.11	0.10	0.11	0.10
20	3.8	0.22	0.11	0.11	0.12	0.10
20	17.1	0.35	0.19	0.16	0.18	0.17
Computed.....		0.328	0.210	0.122	0.222	0.110
Average.....		0.320	0.202	0.118	0.218	0.102
Computed.....		0.320	0.210	0.110	0.215	0.105

Extractions, Percentage

Mesh	Total	On Oxide	Copper	On Sulfide Copper	On Soluble Copper
On 3	65.69	71.5	14.3	71.1
4	76.00	82.2	16.5	81.3
6	82.03	88.8	21.4	88.5
8	85.62	92.3	31.3	91.8
10	86.45	92.8	25.0	93.0
14	87.04	92.4	37.4	92.6
20	87.43	93.0	38.8	92.6
20	83.01	90.2	29.2	90.4
Computed.....	78.50	84.9	27.0	84.3
Average of all ex- tractions.....	78.44				

Note.—The “computed figure” is the assay for the entire sample computed from the weight and assay of each size. The “average” is the arithmetical average of all assays. The “composite” is average of triplicate assays on a carefully composited sample covering the entire year.

As this matter was of much importance, special efforts were made to obtain further data. It was then found that the extractions of the sulfide portion of the ore on separate charges varied considerably from a low of 7 or 8 per cent. on some charges, to nearly 65 per cent. on others. Unusual results were checked and it was found that when the extraction was low the sulfide portion consisted principally of chalcopyrite; while when the extraction was high, the sulfide portion consisted principally of chalcocite. To determine to what extent this was so, selected portions of ore were crushed and screened to pass 4-mesh, but not 6, thoroughly

mixed, and a portion was cut out and analyzed. The original crushed portion was then placed in a perforated sheet-lead box 12 in. square by 6 in. high and embedded in the tank as it was being charged with ore. The box remained therein throughout the leaching and washing cycles, the sample going through all the stages of the usual 5200-ton charge. When the charge containing the lead box had been drained and excavation begun, the box was removed.

Whenever the mine superintendent noticed an unusual quantity of sulfides in the ore, he would advise the laboratory and send a liberal sample of the ore for the box-leaching test. In this manner, it was possible to show, on a somewhat larger scale, that while chalcocite was quite soluble in the lixiviant, chalcopyrite was not.

Occasionally representative specimens of ore about 2 by 3 in. were ground so as to present two smooth faces at right angles to each other. Several of these were then placed in the perforated box and buried in a charge of ore; on the completion of the leach, they were removed from the box, washed and examined. By breaking them at right angles to the face, the depth of solution penetration could be approximately measured. Specimens containing cuprite, chrysocolla, malachite, chalcopyrite and chalcocite were tested in this manner. These specimens also showed that the lixiviant acted quite strongly on all but the chalcopyrite specimens. The solution penetration appeared to be quite uniform for all the material that was leached. The distance of penetration would, of course, vary according to the time the specimens were exposed to the lixiviant and also according to the strength of the latter. In a general way this distance of penetration shows the ideal size to which the ore should be crushed to get the best results.

It is interesting to note that the Inspiration Copper Co. will use a lixiviant practically identical with that used at Ajo, as follows:

	INSPIRATION COPPER CO., PER CENT.	NEW CORNELIA COPPER CO., PER CENT.
Copper.....	2.5 to 3.5	2.0 to 3.5
Free acid.....	3.5 to 7.5	1.0 to 2.8
Ferric sulfate.....	0.0 to 1.0	0.3 to 1.5
Total iron.....	1.5 to 2.5	1.0 to 2.8

Had the sulfides in the mixed ore at Ajo been present as chalcocite and not chalcopyrite, the mixed-ore problems would have been simple and the extraction uniformly high.

The author draws particular attention to the fact that the quantity of iron dissolved per cycle at Inspiration is so small that the discard problem will be unimportant compared with that at New Cornelia. Discard is not carried on only to get rid of iron, but to get rid of all accumulative impurities. At Ajo, these impurities or solvencides (as they are termed by Witherell) per ton of ore leached on a normal 8-day leaching cycle were:

	Pounds
Al ₂ O ₃	12
Fe.....	6
MgO.....	2
CaO.....	1

While comparatively little iron is dissolved from the Inspiration ore during a normal leaching operation, considerable alumina is dissolved; therefore, appreciable discard must be necessary. Due to the simplicity of its determination, in Ajo solutions, iron and not alumina, was used as an indication of the quantity of impurities present. If no iron had been dissolved from the ore at Ajo, the discard would still have been necessary as a larger quantity of alumina than iron is added to the solution during each leaching cycle.

It would be interesting to learn the pounds of solvencides present per ton of ore leached under standard conditions, not only the quantity of iron but the quantities of each of the principal impurities dissolved per ton of ore under the conditions at which the plant will operate. Only when the solution entrained in the discharged tailings contains as much of these solvencides as is dissolved in a like amount of ore would there be no discard.

The author speaks of the peculiar conditions of leaching a charge of quite high-grade ore without dissolving the copper; the same conditions occurred at Ajo during the early test work. This condition first occurred in the 1-ton plant and many weird reasons for it were given. Investigation showed that such charges contained one or more segregated areas of unleached ore. While the areas around these segregated spots were well leached, the outer shell (sometimes 1 in. or more thick) was a deep yellow and quite dense and the interior was unleached ore saturated with copper sulfate solution. These segregations indicated that portions of ore had been surrounded by finely-divided, high-grade material and when the ferric sulfate in the solution came into contact with it a protective coating of hydrated ferric oxide was formed which prevented further solution circulation. The condition also occurred on a number of occasions in the 5200-ton plant while charging tanks under the old system. It is a condition that will not occur with proper charging.

While the reduction of ferric sulfate with sulfur dioxide has not been found necessary by the Inspiration Copper Co., a sulfur dioxide reduction installation will prove a most profitable acquisition, for there may be times when there will not be sufficient sulfides to reduce completely the ferric sulfate and the ampere efficiency will suffer. Acid made by the reduction of ferric sulfate with sulfur dioxide will prove considerably cheaper than acid obtained in any other way. At Ajo, the sulfuric acid was the largest single item of expense and the cost of acid produced in the SO₂ towers was less than half that of chamber-acid. There is no

doubt but that a properly designed and constructed copper leaching plant can be successfully operated by the use of tower acid alone.

The author speaks of the solvent action of the electrolyte on the cathode at the solution line and how this trouble was overcome by the simple use of P. & B. paints. This trouble was experienced at Ajo to such an extent that on one occasion the tank-house foreman reported that approximately 80 per cent. of the cathodes had dropped off the loops. Many preventatives, including P. & B. paint, were tried but the best solution found of the problem was the split loop.¹

The method of circulating the last wash in closed circuit with a precipitation launder is a good plan. This plan also was suggested at Ajo, but was not considered by the management. The original report on the process to be used at Ajo specifically stated that in case of scarcity of water the last wash could be used over again by pumping back the waste liquor from the cementing launders.

It is interesting to note that among other features introduced at Inspiration, it is planned to dissolve the cement copper produced from the discard solution in the tank-house solution. In June, 1915, this plan was recommended as a means of disposing of the cement copper at Ajo. It was tried on quite a large scale, found satisfactory, and its use recommended for the large plant. I am of the opinion that probably over 25,000,000 lbs. of copper have been so treated. To the best of my knowledge this was the first time that this simple chemical reaction had been adapted to any large-scale commercial process. It was also suggested at that time that a special arrangement might be designed by means of which the cement copper sludge could be continually fed into some sort of a diaphragm anode where the freshly-produced ferric sulfate could dissolve it; in other words, to devise a method by which this cement copper could be used as a soluble anode.

G. D. VAN ARSDALE, (written reply to discussion).—I wish to thank those who have taken the trouble to write discussions of my paper describing the Inspiration ferric sulfate leaching tests. As pointed out by Mr. Tobelmann, the method has considerable similarity to that used by the New Cornelia Copper Co. and as finished seems obvious enough and without particular novelty as to the general principles involved. However, where the expenditure of several millions for plant cost is concerned, the apparently obvious cannot be accepted without complete and exhaustive proof, which of course is the reason for the investigation by the company not only of this but also of the other possible methods before the final decision was made.

The statements made by Mr. Tobelmann as to the solubilities of chalcopyrite and other minerals and the methods used for getting this

¹H. A. Tobelmann and J. A. Potter: First Year of Leaching by the New Cornelia Copper Co, *Trans.* (1919) 60, 52. U. S. Letters Patent 1269485, June 11, 1918.

information in the Ajo practice are interesting. Most samples of chalcopyrite I have tested yield at least a part of their copper to ferric sulfate, the percentage varying from 40 to about 60. The solubility of different chalcopyrites varies and evidently that in the Ajo ore is an insoluble type. The average percentage of oxide copper left in the tailings at Ajo is more than the average for the Inspiration tests, which can be explained in various ways. There is of course no real comparison in view of the different ores and conditions.

It is quite correct to say that "had the sulfide in the mixed ore at Ajo been present as chalcocite and not chalcopyrite the mixed ore problem would have been simple and the extraction uniformly high," and it is equally true to say that if we had been unfortunate in having any considerable amount of chalcopyrite in the Inspiration ores the present scheme could not have been used.

I believe the discard problem will not be a serious matter at Inspiration. No discard was required during the entire test period, and the increase in alumina in the liquors did not indicate much probable trouble in this direction. Alumina is not a harmful impurity, does not require the same elaborate control as iron, and is even helpful in electrolysis since it reduces cathode corrosion to an appreciable extent.

As Mr. Tobelmann points out, leaching in this way cannot be done unless there is enough chalcocite in the ore to take the place of the SO_2 used at Ajo. This appears to be the case at Inspiration, but for possible periods of very low sulfide in the ore the expedient of mixing in straight sulfide ores which are available would be simpler than going into the complication of SO_2 reduction. From the standpoint of saving in cost of acid, Inspiration will use 20 lb. of net new acid only per ton of ore, so that the possible saving by making acid by SO_2 would not be large. It is quite true, as Mr. Tobelmann says, that where the acid consumed per pound of copper is not too large a plant can be operated without acid from the outside if SO_2 can be used.

Several other points brought up refer rather more to plant design and operation than to metallurgy and as to these the experience of a year or so will tell us more than can be said now.

C. S. WITHERELL, New York, N. Y. (written discussion).—I note that Mr. Tobelmann has honored me by making use of the word "solventicide" coined by me. As can be gathered by the construction of the word a solventicide is any substance either present in the ore undergoing leaching, or otherwise introduced into the process, that destroys or otherwise renders permanently useless some of the solvent agent. It has the same meaning in general application to leaching as the word "cyanicide" has in the cyanide leaching of gold or silver ores, and therefore if the word solventicide is adopted there would be no further use for the word cyanicide.

The destructive effect of a solventicide may be in the nature of either chemical decomposition or chemical combination, the compounds formed may be either soluble or insoluble; if soluble, steps must be taken to prevent excessive accumulation. It is quite possible for the metal purposely extracted to act as a solventicide with some solvents (e. g., metallic copper with nitric acid).

Next to percentage of extraction, the subject of solventicides will probably be the most important and about the first to be investigated in developing a leaching process for a new undertaking; it even has a bearing on the question of the proper degree of fineness to which the ore should be crushed or ground. Many of the rock-minerals, while appearing to be practically unattacked by the solvent when the particles are over say $1\frac{1}{4}$ in., become perceptibly acted upon when finely ground.

The rational way of expressing the total amount of all solventicides present in any given ore would be in terms of the solvent-agent killed.

In an electrolytic method of metal recovery wherein the accumulated solventicides are eventually disposed of by solution discard, a certain amount of still useful solvent agent must accompany that combined with the solventicides; usually this can be expressed by a factor which is dependent upon the allowable concentration of the solventicides under consideration in the electrolyte.

G. D. VAN ARSDALE (written reply to discussion).—Mr. Witherell's term of "solventicides" is a good substitute for the rather clumsy expressions we have been using. My only criticism is that it is perhaps too general. In our case, for example, we have two active solvent agents, acid and ferric iron. Terminology is not of very great importance, but I think uniformity in the literature should be aimed at, and specific terms used when needed. I am afraid that cyanicide is too well established and too descriptive to be given up.

Perhaps in copper leaching we might consider "antiacid," as a specific term in addition to Mr. Witherell's proposal; since most of our copper leaching is with sulfuric acid, which is not really destroyed or killed. If this term was in use we could say, for example: "The antiacids in such and such an ore are lime, iron and alumina in addition to copper, giving a total antiacidity of 50 lb. of actual H_2SO_4 per ton, of which 30 lb., 2 lb., 8 lb., and 10 lb., are the antiacidities of copper, lime iron and alumina, respectively. Pyrrhotite, which is a solventicide for ferric iron is not present. Pyrite is neither an antiacid nor a solventicide. The antiacid action of the ore can be reduced 5 lb. per ton by not crushing finer than half-inch. The copper sulfide present in the ore is a solventicide for ferric iron, which is remade during the electrolysis." In other words, I would restrict Mr. Witherell's useful new expression, which has the sense of killing or destroying, to substances which actually

do that, and propose the term antacid for those substances which simply combine with an acid solvent.

L. D. RICKETTS, Pasadena, Cal. (written discussion).—A brief history of the leaching experiments conducted by the Inspiration Consolidated Copper Co. prior to the employment of Mr. Van Arsdale may be interesting and may reinforce his valuable paper.

About 8 years ago the Inspiration company constructed a 35-ton test plant for leaching oxidized ores and a long series of experiments were made. It was found a good recovery of copper could be obtained from the thoroughly oxidized ores, but as work progressed it became evident that it would be difficult to mine these ores whose oxide content was too high to permit them being treated economically in our flotation mill.

Tests were then undertaken to treat mixed ores, the plan being to first leach the ore ground to a maximum size of $\frac{3}{8}$ in. and then to grind the tailings from the leaching tanks, after neutralizing with lime water, and recovering the sulfide by flotation. By this dual method very high recoveries were obtained, but it became evident that the cost of the dual treatment was heavy and it was preferable to devise, if possible, a single process through which both the sulfide and oxide content of the ore could be recovered at one and the same time.

It was early determined that an excellent grade of electrolytic copper could be recovered from the sulfuric acid solutions resulting from the treatment of our oxidized ores, and tests were likewise conducted under the direction of engineers from the Anaconda Copper Mining Co. in conjunction with Inspiration engineers for the precipitation of copper with SO_2 gas under conditions of heat and pressure as developed by Van Arsdale many years ago. Very satisfactory results were obtained from these tests, but in the meantime it became more and more apparent that the problem of the mixed ores was very important, and while the success of precipitating copper with sulfurous acid gas was recognized, it was rejected here because this method prevented the presence of ferric sulfate which was known to be a solvent of copper at least.

At this stage a halt was called in the work of our test plant and Mr. Van Arsdale was employed to study the problem of leaching these mixed ores with ferric sulfate and sulfuric acid, and of recovering the copper electrolytically from solutions containing ferrous sulfate and a very high percentage of ferric sulfate, which necessarily had to be regenerated for leaching purposes. Mr. Van Arsdale to expedite matters first undertook laboratory tests in leaching Inspiration concentrates, and having obtained satisfactory results on this material he directed his efforts to leaching the mixed ores direct. He worked out his problem in Los Angeles, first in the laboratory, and later with a small experimental leaching plant, and it was then, as he states, that the 35-ton plant at Inspiration was again started up and I feel that the splendid results obtained redound to the

credit of Mr. Van Arsdale, Mr. Aldrich, Mr. Scott and the other gentlemen associated with them in the work.

G. D. VAN ARSDALE (written reply to discussion).—In conclusion, I would say that while the paper was written under my name as author by instructions of Dr. Ricketts; as he has pointed out, my part of the work was only coordinate with that of the others concerned. Since it was "committee" work throughout, the method should properly be called the Inspiration process since the results obtained were not individual but a result of this policy and the splendid cooperation of all engaged in the work.

Production of Ferric Sulfate and Sulfuric Acid from Roaster Gas*

BY G. L. OLDRIGHT, H. E. KEYES, AND F. S. WARTMAN,† TUCSON, ARIZ.

(Salt Lake City Meeting, September, 1925)

THE economic manufacture of sulfuric acid by the ordinary chamber process usually involves production on a large scale and a plant that is costly to construct. The nature of sulfuric acid makes it costly to transport any great distance. For these reasons, the metallurgist has not found it feasible, at times, to beneficiate ores amenable to leaching, and a need exists for a local process that will produce acid cheaply on a small or large scale.

To leach ores containing residual sulfides, an oxidizer, such as ferric sulfate, is needed in solution. Precipitation with scrap iron is one of the cheapest methods of removing some metals from solution, giving a plant of low first cost and supplying a source of cheap ferrous sulfate. The other ingredient needed for the process is SO_2 roaster gas, the addition of which, as described below, will give both ferric sulfate and sulfuric acid. Where roaster gas is a waste or obnoxious product, the expense for materials is still further lessened. The use of ferric sulfate and sulfuric acid as a solvent lends itself well to the utilization of scrap iron as a precipitant, and the stages of the process fit in well together as an economic whole.

APPLICATIONS

The hydrometallurgist usually thinks of ferric sulfate as a partial solvent for some of the sulfides of copper alone, as most work has been done on this metal. The processes of Hannay and Christensen, for leaching unroasted galena with ferric chloride made by anodic oxidation, show the added solvent action given by "ic" salts when added to brine solutions. It was found by R. D. Bradford (in some work to be published soon by the University of Utah) that, by the addition of a ferric salt to a brine solution, the silver as well as the lead in an unroasted semi-oxidized ore could be largely dissolved. The "ic" salt in the case of silver has evidently the same effect as the case of cupric sulfate when

* Published by permission of the Director, U. S. Bureau of Mines.

† Hydrometallurgist, Associate Metallurgist, and Junior Chemist, respectively, Southwest Experiment Station, Bureau of Mines.

used with the old Russell "hypo" process. Ferric sulfate has also been used in leaching ores of zinc and nickel, although the solvent action on the sulfides of these metals is probably slow. In many processes, it is desired to oxidize ferrous sulfate to facilitate the removal of the iron, either before purifying the solution when this is an objectionable impurity, or in order that the precipitated ferric hydrate made by rendering the solution basic may drag down with it other substances such as compounds of arsenic or antimony. Where the content of certain impurities in the solution is not too great, such oxidation of the iron may be readily carried out.

The advantages of acid ferric sulfate over dilute sulfuric acid as a leaching agent for mixed copper ores have long been realized. The fact that one company is now engaged in constructing a six million dollar leaching and reduction plant involving the use of acid ferric sulfate is sufficient evidence that a cheap and efficient method of producing this solvent should warrant the attention of the hydrometallurgist. Anodic oxidation of ferrous sulfate has found favor where the magnitude of operations or a cheap source of power justify electrolytic precipitation. However, in cases where electrolysis is not feasible, attempts have been made to oxidize ferrous sulfate solutions by various means. A noteworthy example was the work at Cananea.¹

"The materials treated at Cananea consisted of mill tailing sand and of flue dust from the furnaces." These products are two for which leaching with cheap ferric sulfate-sulfuric acid is still applicable. The leaching in place of copper-bearing material, in general, whether in dumps or stopes, leaching by percolation in vats, or the leaching of low-grade and finely ground material, as outlined by Leaver,² are all fields that have been contemplated for the process.

PREVIOUS WORK ON MAKING FERRIC SULFATE

It is obvious that in the oxidation of neutral ferrous sulfate sulfur must be supplied as sulfate radical, otherwise a precipitate of basic ferric sulfate will form. A mixture of sulfur dioxide and air, such as is furnished by the roasting of pyritic ore or the burning of sulfur, furnished the necessary constituents for such oxidation. The first work, within the knowledge of the authors, in which sulfur dioxide and air were used in producing acid ferric sulfate in the United States, was carried out by chemists at the Clifton smelter of the Shannon Copper Co. in 1912.³

¹ W. L. Austin: Leaching of Copper Ores. *Mines and Methods* (Sept., 1910).

² E. S. Leaver and R. V. Thurston: Ferric Sulphate and Sulphuric Acid from Sulphur Dioxide and Air. Bur. of Mines Report of Investigation, Ser. No. 2556; O. C. Ralston: The Ferric Sulphate-Sulphuric Acid Process. Unpublished report of the Bureau of Mines.

³ W. A. Sloan and F. W. Rose: Private communications.

The object of this work was to develop a process for treating the oxidized ores of the Shannon Copper Co. Because of excessive lime in the ore, acid leaching was abandoned in favor of sulfating by roasting with pyrite followed by a water leach. A typical experiment carried out by F. W. Rose in 1912, at this plant, is given. A solution containing 12.8 gm. per liter ferrous sulfate was treated with smelter-stack gas to saturation, after which air was blown in slowly until the odor of sulfur dioxide was not perceptible. This procedure was repeated four times and the solution assayed for ferric iron; it was found to contain 1.6 gm. per liter ferrous sulfate and 10.7 gm. per liter ferric sulfate. Furthermore, free sulfuric acid was found to be present, although an exact determination of acid was not made.

Work by van Barneveld and Leaver,⁴ and their associates in the direct leaching of copper ores with sulfur dioxide showed that sulfuric acid could be formed by treating a ferrous sulfate solution with sulfur dioxide and air.⁵ The various factors governing the reactions involved have since been made the subject of an extended investigation.⁶

The development of a commercial process for producing dilute sulfuric acid is now in progress at the Southwest Experiment Station of the Bureau of Mines. It is the purpose of this paper to give a report of recent progress in the commercial aspects of the process which have not had publicity to date.

The main end reactions involved may be represented as follows:



The gas, containing about 4 per cent. sulfur dioxide and not less than 15 per cent. oxygen, is introduced into a ferrous-sulfate solution by means of a suitable aerating device. For best results, the solution should contain from 4 to 20 gm. per liter iron. One essential condition for efficient operation with a rich gas is the subdivision of the gas into bubbles of 1 to 2 mm. diameter. Under proper conditions, reaction (1) takes place nearly to completion after which the sulfur combines according to reaction (2). Table 1 gives results obtained using a flat wool fabric aerator. Pure sulfur dioxide gas was withdrawn from a cylinder and mixed with air.

In Table 1, as well as in subsequent work, the sulfur used in oxidizing iron was converted to the equivalent sulfuric acid and thus used in the calculations for aeration rate and rate of acid formation. The ferrous sulfate used in all this work was a crude crystallized product from the

⁴ C. E. van Barneveld and E. S. Leaver: Leaching Non-sulfide Copper Ores with Sulfur Dioxide. Bur. of Mines *Tech. Paper* 312.

⁵ E. S. Leaver, U. S. Pat. 1477965, 1923.

⁶ E. S. Leaver and R. V. Thurston; O. C. Ralston. *Op. cit.*

TABLE 1.—*Data, Using Aerator of 121 Sq. Cm. Cross Section*

Ferrous iron at start of run = 5.0 gm. per liter; mixture of pure sulfur dioxide and air used

Run No.	SO ₂ Per Cent.	Column Height, Cm.	Hours Aerated	Final Acidity, Gm. per Liter	Aeration Rate*	SO ₂ Efficiency (for 5 Per Cent. Acid)
191	5.0	60	5½	50	2.3	98.8
192	5.0	60	2½	37	3.7	90.0
182	5.5	80	6½	55	1.95	99.0
185	5.8	80	4	58	3.3	99.0
186	5.2	80	2½	53	4.5	99.0
196	5.0	100	6½	59	3.0	99.0
200	5.0	100	6	63	3.9	99.5
201	5.0	100	4	50	4.95	99.0
202	5.0	100	3½	57	6.4	99.0
205	5.0	140	5	53	6.0	96.5

*Cubic feet free gas per square foot aerator surface per minute.

scrap-iron discard solution at the leaching plant of the New Cornelia Copper Co.

PRODUCTION OF ACID FERRIC SULFATE FROM ROASTER GAS

After obtaining the foregoing results, the authors gave attention to the commercial aspects of the process. Simplicity of operation and low production costs consistent with high efficiency of sulfur-dioxide utilization were given first consideration. Regardless of the details of the process adopted, it was considered that the source of sulfur dioxide would most likely be pyritic ore roasted in standard equipment of the multiple-hearth type, although pure sulfur could be burned in appropriate apparatus if conditions warranted. A survey of several typical roaster installations at copper smelters in the Southwest showed the following:

FURNACES SELF-ROASTING

	PER CENT.
Sulfur in heads.....	30.5
Sulfur in calcine.....	11.3
Sulfur dioxide in gas.....	4.0
Oxygen in gas.....	15.0

Therefore, when utilizing waste roaster gases, or in a new roaster installation, a gas containing 4 per cent. sulfur dioxide and 15 per cent. oxygen would most likely be produced.

When considering the metallurgical steps involved in the process, two possibilities were apparent. The sulfur dioxide might be absorbed in towers through which the solution circulated from porous bottom cells. Air blown through the porous bottoms should fix the dissolved sulfur

dioxide and, by continued circulation through towers and fixing cells, the desired reactions should be brought about. However, when fundamental principles were considered, this scheme did not appear so attractive. The solubility of sulfur dioxide in water is nearly proportional to the partial pressure, or percentage sulfur dioxide, in the gas. Also the presence of acid or dissolved salts is likely to affect the solubility. Comey⁷ gives the solubility of sulfur dioxide in water as 2.28 gm. per liter at 50° C., the partial pressure of sulfur dioxide being 30.5 mm. mercury. This corresponds to about a 4 per cent. sulfur dioxide gas under Tucson conditions and, as 50° C. is approximately the operating temperature, this figure may be used as a basis of calculation. Experimental work verified Comey's figure and also showed that increasing concentration of sulfuric acid decreased the solubility. A 4 per cent. gas showed 1.6 gm. per liter sulfur dioxide soluble in a solution containing 50 gm. per liter sulfuric acid at 50° C. The presence of ferrous iron caused erratic results. Tentative calculations indicated considerable pumping cost for solution circulating through towers. Some advantage might be gained using mechanical absorbers,⁸ but it seemed advisable to first investigate the second possibility; namely, a method of directly introducing the gas into the solution.

While the details of a commercial process had not been previously worked out, there was one point on which the various metallurgists apparently agreed; namely, that the direct blowing of a dirty gas through a porous medium was precluded on account of clogging the interstices. No data, however, were at hand to show whether the ordinary dust-collecting systems would clean the gas sufficiently without wet scrubbing. Dry roaster gas may be handled in iron pipes with very little corrosion if the temperature is maintained at 200° F. or above. Scrubbing the gas with water would necessitate expensive acid-proof construction of the scrubber and some conveying equipment, at least. By giving the gas only a rough cleaning, as obtainable with settling chambers or cyclones, it was estimated that the amount of flue dust carried against the surface of the porous aerator would be approximately 0.5 lb. per sq. ft. per 24 hr. To test this point experimentally, flue dust (−200 mesh) was mixed with air and blown into an aerator of 121 sq. cm. cross section, equipped with "Duro" cloth fabric. Ordinarily, a pressure drop of 0.5 lb. is caused by the cloth with clean gas at an aeration rate of 4 cu. ft. per sq. ft. aerator surface per minute. The introduction of dust at 6 lb. per 24 hr. per square foot aerator surface, which is twelve times the rate expected in practice, increased the pressure 1 lb. in 45 min. The pressure

⁷ A. M. Comey: "A Dictionary of Chemical Solubilities." Macmillan Co., New York.

⁸ Wm. E. Greenawalt: U. S. Pat. 1528204, 1925; N. C. Christensen: Pat. 1462363, 1923.

would return to its original value by shutting off the flow of air and allowing the solution to "back flush" through the single cloth for a few seconds. As no serious clogging was observed, unless several superimposed blankets were used, this scheme offered a possible efficient method for aerating ferrous-sulfate solutions with roaster gas on a semicommercial scale.

Aside from the fabric aerator, several other types have been recommended for this work, but experimental data are incomplete to date. Brief mention, however, will be made of certain meritorious designs.

Rotating Shear Bubbler

The production of small bubbles on a commercial scale by utilizing the shearing action of a revolving cylindrical device pierced with $\frac{1}{32}$ -in. holes through which the gas passes into the solution was advocated by Greenawalt about 1915.⁹ In 1924, C. G. Maier¹⁰ experimented with a similar apparatus and made accurate measurements on the relation of size of bubble to diameter of orifice, gas velocity, pressure, and speed of solution flow normal to the orifice. This work of Maier led to an aeration device, known as the "grid type" aerator, consisting of lateral pipes accurately spaced 0.01 in. apart, the gas being discharged through holes $\frac{1}{32}$ in., or smaller, in diameter located slightly above the plane of axes of the pipes. Solution forced through the slots between the pipes causes a shearing action, thus producing bubbles of approximately the same diameter as the orifice. Without such shearing action, the bubble diameter is about ten times the orifice diameter.

Another type has been developed by Greenawalt¹¹ and tested to a limited extent by the Southwest Experiment Station with encouraging results. The gas is introduced from the bottom of the tank into the center of an impeller having hollow vanes. Some solution mixes with the gas passing through the impeller and the gas is subdivided into very fine bubbles as it is thrown out by the centrifugal force. This type of apparatus lends itself to excellent control as the impeller speed and rate of gas flow may be adjusted to suit conditions. Advantages of this design are freedom from possibility of clogging by dust and low gas pressure required, there being a slight suction effect produced at the impeller. Possible disadvantages are high power consumption and the difficulty of obtaining uniform gas distribution in a tank of large cross section.

Of all the factors dealing with this process, fineness of bubble size has probably been considered of prime importance. In the experimental laboratory work, it was frequently noted that shortly after the completion of the oxidation stage the bubble size would increase, sometimes to five times the original diameter. This was not because of any change in

⁹ Wm. E. Greenawalt: U. S. Pat. 1374500.

¹⁰ C. G. Maier: Unpublished report, Bureau of Mines.

¹¹ Wm. E. Greenawalt: U. S. Pat. 1374445 and 1374446, 1921.

conditions of operation as far as could be observed; further investigation disclosed that the cause of the trouble was coalescence. It was a simple matter to construct an aerator capable of producing small bubbles, but the prevention of coalescence was another problem. Further research along this line was necessary, the details of which will be offered for publication in the near future. Many substances were found, small quantities of which inhibited coalescence to some extent; among these may be mentioned ferrous sulfate, glue, and pine oil. Such substances have few properties in common and it is apparent that the laws governing coalescence are very complex. It was found that coalescence was not directly dependent on the magnitude of the static surface tension of the solution.

Recent investigations at Tucson¹² indicate that when using gas of very low concentration of sulfur dioxide, the small bubble loses its advantage and larger bubbles give more efficient oxidation. Furthermore, for each bubble size, the rate of addition of sulfur dioxide being constant, there is a definite concentration of sulfur dioxide at which the maximum rate of oxidation takes place, this concentration being higher with the smaller bubble sizes. The foregoing indicates that by blowing in auxiliary air with the roaster gas, larger bubbles than 1 to 2 mm. diameter would not only suffice, but would actually result in a higher sulfur-dioxide efficiency than in the case of the smaller bubbles.

DESIGN AND OPERATION OF PILOT PLANT

To demonstrate the commercial possibilities of producing acid ferric sulfate from roaster gas, a pilot plant was constructed at the Tucson station, in which additional data have been secured which may serve as a basis for larger scale construction and operation. Much work in testing various forms of aerating devices, in the hope of making possible improvements remains to be done, but on account of the successful results obtained thus far, the data at hand are herein presented. The steps involved were reduced to their utmost simplicity and consisted of roasting with a standard type multiple-hearth roaster, rough cleaning the gas in a novel dust collector, and blowing by means of a cycloidal blower into a porous-bottom aerating column.

Roaster

Pyrite from the Jerome district was roasted in a six-hearth, 2 ft. diameter, gasoline-fired Herreshoff roaster having air-cooled rabble arms. On account of high radiation losses, such a small furnace was not self-roasting; and as it was found that direct firing lowered the oxygen content of the gas about 4 per cent., which prevented satisfactory oxidation of the solution, indirect heating was obtained by passing the air from

¹² Wm. A. Jennings: *The Effect of Bubble Size on the Optimum Sulfur Dioxide—Air Ratio in the Ferric Sulfate—Sulfuric Acid Process*. Thesis, University of Arizona, 1925.

the cooling arms into a pipe through a combustion chamber and discharging the preheated air on to a lower furnace hearth; this functioned very satisfactorily.

Dust Collector

The furnace gas was cleaned and cooled in a Reverse Nozzle Dust Collector, manufactured by the By-Products Recoveries Co., Inc. This is a stationary all-metal apparatus and is claimed to effect a clearance comparable to an electrostatic precipitator. Since its installation, there has been no trouble because of increase of gas pressure against the aerator cloth.

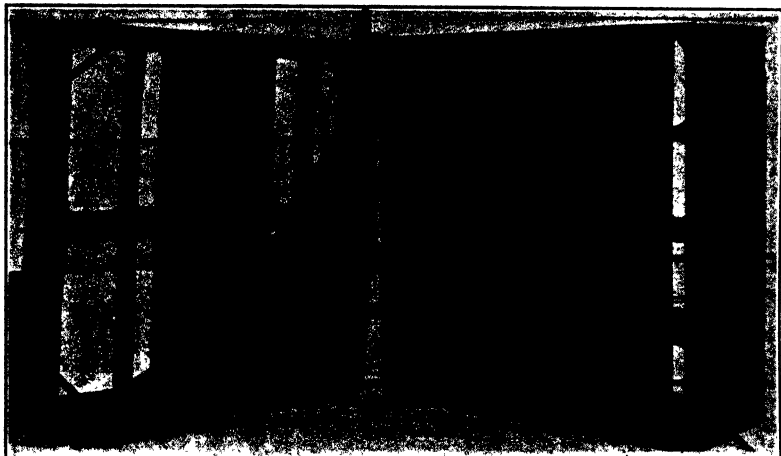


FIG. 1.—AERATOR GRID SUPPORTING "DURO" CLOTH DIAPHRAGM, WITH CLOTH ROLLED BACK TO EXPOSE PARTS, AND CRATE WHICH RELIEVES TENSION ON THE CLOTH; 12-IN. BAFFLE BOARDS IN CENTER ARE PLACED OVER GAS-INLET PIPES IN BOTTOM OF AERATOR TANK TO SPLIT GAS STREAM; CLOTH IS STRETCHED ACROSS FRAME BY BEING FORCED BY WOODEN STRIPS INTO GROOVE SHOWN IN SIDE; STRIPS ARE HELD IN PLACE BY LONG WOODEN WEDGES FITTING AGAINST SIDE OF AERATOR, WHEN DIAPHRAGM IS HORIZONTALLY IN PLACE IN BOTTOM OF AERATOR TANK.

Blower

For blowing the gas, a Connersville gas pump, size 20B, rated at 46 cu. ft. per min., free air at 4 lb. pressure was used. In most tests, the rate of gas flow was about 25 cu. ft. per min. Although the blower has not been operated long enough to furnish conclusive data on corrosion effects, no trouble has been observed to date. Iron blowers of the Root type have been operated for years handling SO_2 gas for the Hargreaves process.¹³

Aerator

From the blower, the gas passes in a 2-in. iron pipe, through an orifice meter, to the aerator; lead pipe is used from the point where the

¹³ Lunge: "Sulphuric Acid and Alkali," 2. 246, 3d ed., Gurney & Jackson, London.

solution level is reached. The aerator tank is $7\frac{1}{2}$ ft. high and has a cross section of 7.22 sq. ft. The aerator surface is 6.67 sq. ft., the fabric being secured in the tank without any metal parts. "Duro" cloth has been used as a porous medium, but the laboratory tests have shown that any closely woven, heavy woolen cloth will serve the purpose. Figs. 1 and 2 show aerator details. To date, all the runs have been carried out

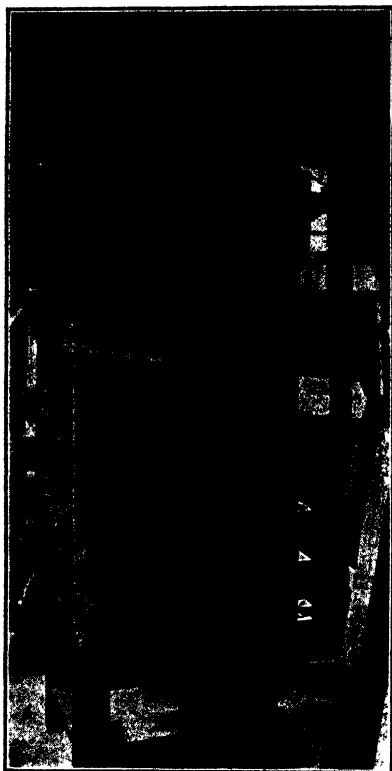


FIG. 2.—CONSTRUCTION OF AERATOR TANK; NOTE JUNCTION OF IRON WITH LEAD PIPE LEADING GAS OUTSIDE AERATOR DOWN UNDER ITS BOTTOM, AND HEAVY REINFORCING AT BOTTOM OF CELL.

by the batch method, although the process can readily be made continuous by passing the solution through a number of aerating cells in series.

PILOT-PLANT DATA

A number of successful runs have been made, examples of which are shown in Table 2. In the early work on this process, it was considered essential that no appreciable free acid be present during the oxidation stage. Run No. 6 shows that the ferrous iron was completely oxidized

with an initial acidity of 14.6 gm. per liter, the efficiency of sulfur dioxide for the entire run being 96 per cent.; however, 1.3 gm. per liter of ferric iron were initially present.

The length of life of a "Duro" cloth aerator is still a mooted question. The 121 sq. cm. aerator has lasted through 25 runs, averaging 5 hr., each and at this writing has apparently not deteriorated. When the lateral dimensions of such an aerator are increased, however, mechanical stresses on the cloth must be reckoned with; otherwise, stresses will occur in the fabric, causing an increase in the size of interstices, thus allowing uneven air distribution and larger bubbles. This danger has been largely overcome by setting a lattice-shaped framework over the cloth. Uniformity of material must also be insisted on for satisfactory results.

TABLE 2.—*Pilot-plant Production of Acid Ferric Sulfate with Roaster Gas*
Height solution column, 130 cm.; volume solution, 872 liters; gas pressure at aerator, 2.2–3.2 lb. per sq. in.

Run No.	Composition of Solution, Grams per Liter					Gas Analyses, Per Cent.			Hours Aerated	Efficiency, Sulfur Dioxide Per Cent.	Aeration Rates	Rate of Acid Formation ^b	Rate of Acid Formation ^c
	Acid at Start of Run	Total Iron	Iron Oxidized	Ferrous Iron End of Run	Acid Produced	Ingoing		Out-going					
						Sulfur Dioxide	Oxygen	Sulfur Dioxide					
3	0.3	4.4	4.2	0.15	58.2	3.17	15.3	0.19	12.0	94	3.4	5.1	1.42
4	nil	6.0	5.4	Tr.	54.3	3.16	15.0	0.13	10.4	96	3.8	5.7	1.64
5	nil	4.9	1.8	2.7	22.1	5.03	11.7	1.30	6.8	74	1.77	3.24	0.95
6	14.6	5.1	3.8	Tr.	39.4	4.08	14.3	0.15	8.5	96	3.45	6.7	1.91
8	nil	5.7	5.7	Tr.	49.5	2.16	16.8	0.02	7.7	99	4.64	5.54	1.41
9–12 ^d	nil	5.1	3.8	0.3	76.0	1.43	17.6	0.50	33.0	65			

^a Cubic feet free gas (700 mm. Hg. and 30° C.) per square foot aerator surface per minute.

^b Grams sulfuric acid per liter per hour over entire run.

^c Pounds sulfuric acid per square foot aerator surface per hour.

^d This run was carried out on four different days, loss by leakage being made up by adding water and ferrous sulfate.

To date no expression has been formulated for the permissible ratio between oxygen and sulfur dioxide content of the gas. This relationship appears to be a rather complex function. It was found difficult to obtain satisfactory oxidation in the pilot-plant solutions with an oxygen content below 13 per cent., even though the sulfur dioxide was considerably less than 3 per cent. This is interesting, in view of the fact that excellent results were obtained in a similar, but smaller scale apparatus, using a mixture of sulfur dioxide and air of 5 per cent. sulfur dioxide and 19.5 per cent. oxygen. It is thus evident that the permissible $\text{SO}_2:\text{O}_2$ ratio is not a constant quantity.

PRODUCTION OF FERRIC SULFATE AND SULFURIC ACID

APPLICATION OF PROCESS TO TREATMENT OF CUPRIFEROUS PRODUCTS

The aim of these investigations has been to assist the copper hydro-metallurgist in producing an inexpensive and satisfactory leaching solvent. It is hoped, within the coming year, to extend this work to the semicommercial treatment of typical ores by the Bureau of Mines process. Preliminary work has already been undertaken on products from one of the representative southwestern copper companies. It is desired to produce acid ferric sulfate from the solution discarded at the scrap-iron boxes and to utilize this solution for leaching a large dump. The discard solution contains:

	GRAMS PER LITER
Total iron.....	20.2
Ferrous iron.....	19.7
Sulfate, SO ₄	69.5
Copper.....	trace

The theoretical sulfate required to combine with the iron would be 35.1 gm. per liter.

Evidently these solutions are very foul with sulfates and experimental evidence was necessary to determine whether the iron could be oxidized as efficiently as in former tests with purer solutions. Accordingly, tests were run in the apparatus used for obtaining the data of Table 1. The results compared favorably with a similar test, using crude ferrous sulfate crystals as in the regular runs; Table 3 shows the comparison.

TABLE 3.—*Production of Acid Ferric Sulfate Using Pure Sulfur Dioxide and Air; Comparison of Plant and Synthetic Solutions*

5 per cent. sulfur dioxide; 19.5 per cent. oxygen; aerator, 121 sq. cm.; height of column, 100 cm.

Solution	Assay Solution, in Grams per Liter						Efficiency Sulfur Dioxide Per Cent.	Number Hours Run
	Total Iron	Total Sulfate (SO ₄)	Sulfate Required for Iron	Acid Produced	Iron Oxidised	Ferrous Iron End of Run		
A	21.0	57.2	37.3	28.7	19.0	0.6	91	4
B	20.2	69.5	35.1	24.0	17.2	2.5	87	4
C	4.0			12.4	3.95	nil	100	1.25

A, solution made up from Ajo crude ferrous sulfate crystals.

B, iron-box discard solution as obtained from leaching plant.

C, same as solution "B" but diluted to concentration shown.

The data show that the excess sulfate probably affects the efficiency adversely, but that if these plant solutions are diluted, results may be obtained equally as good as with the solution made from the crude ferrous sulfate crystals.

SOME FACTORS INVOLVED IN COMMERCIAL-PLANT DESIGN

Pilot-plant data having been given showing that ferrous-sulfate solutions may be successfully oxidized by roaster gas, using a fabric-type aerator, attention will now be turned to certain features of design and operation of a plant of commercial dimensions. The following calculations are based on semi-commercial results obtained, but are at best only tentative as no large-scale plant has been built.

Materials of Construction

Ordinary iron construction has been found satisfactory for blower and piping to the point where the temperature drops below about 200° F., beyond which lead should be used. The corrosive property of the gas is largely dependent on its moisture content, therefore the sulfide ore to the roaster should be as dry as possible and direct firing of hydrocarbon fuel should be avoided.

Aerator Tanks

Unpainted redwood has been used in the pilot plant. It has been noted that when solutions were aerated in such tanks the bubbles coalesced badly after a short time, presumably on account of extracting some substance from the wood. This has been rectified by using suitable addition agents. A coating of acid-proof paint would doubtless be advantageous, or better still, a lead lining. The porous bottom in each cell should be divided into several independent compartments, each connected to the gas line by a shut-off valve. Any irregularities that might develop in the porous medium could then be compensated by adjustment of the gas valves. The cells should be supplied with hoods leading to the outside atmosphere, as the air discharged would be deficient in oxygen even though sulfur dioxide were not present in appreciable quantities. No work has been done on producing the acid solution by a continuous process, but this could be accomplished by several cells in series.

Roasters and Dust Collectors

This portion of the process should not deviate from standard practice. Experience has shown that the oxygen content of the gas should not be lower than 15 per cent., and it has been found that standard self-roasting operations will produce 4 per cent. sulfur dioxide and 15 per cent. oxygen. Wet scrubbing of the gas is neither necessary nor desirable, only such cleaning being required as can be done easily and cheaply.

Blowers

No particular make of blower is recommended; several types on the market have been investigated and appear to meet the requirements.

On account of dust particles in the gas, a machine having considerable clearance would be preferable.

Size of Units

To arrive at tentative figures for cost of construction and operation, calculations will be made showing the size of equipment required for producing the equivalent of 20 tons of 100 per cent. sulfuric acid per 24 hr., an amount sufficient to leach approximately 1000 tons of 1 per cent. copper ore, if 2 lb. of acid are consumed per pound of copper.

Table 2 shows an average of the equivalent of 1.47 lb., of 100 per cent. sulfuric acid produced per hour per square foot aerator surface, and the authors have reason to believe that this figure will be considerably increased with improvements in the manner of operation. Taking 1.25, to allow a factor of safety, there would be produced roughly 30 lb. acid per square foot per 24 hr.; 40,000 lb. acid per 24 hr. would require 1333 sq. ft. of active cloth area. Assuming 90 per cent. of the cell bottom to be active surface, the total cell area would be 1481 sq. ft. Figuring each cell to be 4 ft. wide by 40 ft. long, practically ten cells would be required, which is in all probability an outside figure.

Twenty tons of acid is equivalent to 6.53 tons of sulfur, a quantity that would easily be handled by a single roaster unit of the six-hearth, 23-ft. diameter size. At a typical roaster installation, each furnace roasts 33 tons of pyritic copper ore containing 43 per cent. sulfur and produces a calcine of 5 per cent. sulfur, the ore being crushed to $\frac{1}{4}$ in. Each roaster removes about 12.5 tons of sulfur.

At 25° C., and 700 mm. mercury, 1 cu. ft. of pure sulfur dioxide weighs 0.1545 lb.; therefore, 6.53 tons sulfur per 24 hr. would be equivalent to 2935 cu. ft. of 4 per cent. sulfur dioxide gas per minute. The aeration rate would be 2.2 cu. ft. per square foot aerator surface per minute, based on 100 per cent. efficiency of sulfur dioxide. At 90 per cent. efficiency the aeration rate would be 2.45. A typical flotation installation of the Southwest uses an aeration rate of 5, so the calculated figure is very conservative.

Costs

In the construction of a plant, a major consideration would be the balancing of initial expense against operating cost. In the foregoing, a column height of $4\frac{1}{4}$ ft. was assumed. By increasing the column height, the aeration rate may be raised considerably without loss of efficiency. This means less floor space and cheaper construction, but greater power requirements. One of the large concentrators uses 275 hp. to blow 10,000 cu. ft. free air per minute, the pressure being 4.5 lb. per sq. in. On this basis 82.5 hp. would be required for 3000 cu. ft. per min. which equals 61.5 kw. With power at $1\frac{1}{2}$ cents per kw.-hr., the blowing cost would be

\$22.20 per 20 tons acid or \$1.10 per ton. The roasting cost is problematical, owing to variable conditions at different plants. If high-grade concentrates produced at the property are roasted, the saving in freight to the smelter may offset the roasting cost and little or no charge would be made against the acid for roasting. If iron pyrite is purchased, shipped in, roasted, and then discarded, the cost may be estimated at \$6 per ton pyrite. Assuming that one-third of the total weight of pyrite equals the sulfur converted to sulfuric acid, the cost would be \$5.88 for pyrite, including roasting, per ton of 100 per cent. sulfuric acid. The labor cost for the aeration division should not exceed \$1 per ton acid. Interest, depreciation, and repairs on a \$50,000 investment would be about \$1.50 per ton acid, making a total cost per ton 100 per cent. acid as follows:

	WITH ROASTING CHARGE	WITHOUT ROASTING CHARGE
Roasting and purchase of pyrite.....	\$5.88	
Aeration, power.....	1.10	\$1.10
Aeration, labor.....	1.00	1.00
Depreciation and amortization.....	1.50	1.50
Total.....	\$9.48	\$3.60

Considering the small operating cost, relatively low first cost, and the fact that the process lends itself to comparatively small-scale installations at isolated points, it is believed that a contribution has been made to the methods for metallurgical treatment of low-grade leachable copper ores.

SUMMARY

1. A study of the commercial aspects of the ferric sulfate—sulfuric acid process has been made by the Southwest Experiment Station of the Bureau of Mines.

2. Laboratory tests in producing acid ferric sulfate from sulfur dioxide-air mixtures and ferrous sulfate solutions have been confirmed by pilot-plant runs in which roaster gas was used to aerate solution in 1-ton lots.

3. Using a 4¼-ft. column of solution, acid up to 55 gm. per liter was produced at the rate of over 5 gm. per liter per hour at an efficiency of sulfur dioxide of 94–99 per cent.

4. Acid ferric sulfate has been successfully produced from leaching-plant scrap-iron discard solutions.

5. Aerators of the porous fabric type have given satisfaction in this work.

6. Based on the Tucson pilot-plant results, the costs for acid of a strength up to 50 gm. per liter should be from \$4 to \$10 per ton, depend-

ing on pyrite cost, for a plant producing 20 tons of 100 per cent. sulfuric acid per 24 hr.

ACKNOWLEDGMENTS

To the early workers on the ferric sulfate-sulfuric acid process and to the operators of the Southwest copper properties who lent their cooperation in furnishing data on their plants, the authors wish to express their appreciation. A complete historical account by Mr. O. C. Ralston of the development of the whole process is soon to appear in a Bureau of Mines publication.

DISCUSSION

G. D. VAN ARSDALE, Los Angeles, Calif. (written discussion).—Years ago, Dr. James Douglas produced ferric iron (together with acid) on a large scale by blowing dilute SO_2 through chloride liquors. In published accounts, he called attention to the ease with which solutions could be reduced or oxidized, or large amounts of dilute acid made in this way. So far as I know, the first large-scale tests using these principles for sulfate solutions were, as stated in the paper, made for the Shannon Copper Co. F. Schimerka should have been mentioned in connection with these experiments, as he was in charge of the leaching.

The authors, on page 85 say:

a cheap and efficient method of producing this solvent should warrant the attention of the hydrometallurgist. Anodic oxidation of ferrous sulfate has found favor where the magnitude of operations or a cheap source of power justifies the electrolytic precipitation.

As the electrolysis cost for precipitating copper is chargeable entirely against the copper made, ferric iron made by anodic oxidation not only costs nothing, but should be credited with voltage reduction, possible to a considerable extent. It is difficult to see how a cheaper and more efficient method for making ferric iron can be devised than one that has no charge against it.

The feasibility and relative economy of electrolytic precipitation are conditioned more by the grade of material being leached and the obtainable strength of solution than by magnitude of operation and power cost, as stated by the authors. It is not feasible to precipitate electrolytically from mine waters or heap leaching solutions, because of their extreme dilution; but because of this dilution it would not be practicable to make ferric iron and acid from such solutions by roaster gas. It has been demonstrated that stronger solutions, say with 1 per cent. or less, can be stripped electrolytically at a smaller cost than is possible by iron precipitation. The cost of power, of course, is important, but in the Southwest where location and freight rates would allow the use of acid at a cost of \$10 per ton, and the bringing in of iron at a reasonable cost, oil could be brought in and power produced at a reasonable cost. The same

thing applies to a low enough fuel cost to permit of making iron locally.

For anything except the very weakest solutions, there is no doubt whatever as to the relative economy of electrolysis as against cementation. Generally speaking, in the Southwest, where iron can be delivered for 1 to $1\frac{1}{4}$ cents a lb., power can be made for $1\frac{1}{2}$ cents per kw.-hr. It takes roughly $1\frac{1}{2}$ lb. of iron to precipitate 1 lb. of copper, and $\frac{3}{4}$ lb. per kw.-hr. direct current is conservative. A cost comparison of the two precipitation methods, therefore, would be as follows:

ELECTROLYSIS		CEMENTATION	
Power.....	\$0.02	Iron.....	\$0.015
Labor.....	0.006	Labor.....	0.015
		Treatment....	0.01
		Refining.....	0.0125
		$1\frac{1}{2}$ lb. acid @ 12 c.....	0.0075
Cathodes.....	\$0.026	Refined copper.....	\$0.06

Freight East and selling are not charged in either case. The average labor cost of making cement copper, in the Southwest, has been higher than the figure given. Treatment cost of the cement at the smelter is assumed at 1 cent, probably it will not be less than this.

It is fair for comparative purposes to charge cementation with the $1\frac{1}{2}$ lb. of acid that is regenerated by electrolysis. Evidently under these conditions cementation means a copper cost for precipitation of nearly three times electrolytic costs. Where leaching is at all possible, and solutions of say 1 per cent. or better are obtainable, this large difference would amortize the relative plant costs quickly enough to make an electrolytic plant a very desirable investment. If the production of copper by cementation was equally cheap, the Southwest long ago would have been dotted with acid leaching and iron precipitation plants. The production of ferric sulfate and acid by the method described necessitates iron precipitation, therefore the method can have only limited application, as electrolysis is much cheaper than cementation, except for very dilute solutions or possibly for remote localities where neither would be possible. It is a simple matter to throw a lot of acid on to a batch of ore, drain this off, and precipitate the copper by iron; but this method will pay only under very exceptional conditions.

Using the term pilot plant for the small-scale apparatus used in the tests is misleading. Most persons would define a pilot plant as one in which full-size apparatus in all details is used in the smallest number of units possible, and from which complete, definite, reliable information as to operation and costs are obtainable. The proper steps for any important investigation are: laboratory work, test-plant investigation in small-scale working apparatus, and pilot-plant operation in full size. The scale of this work belongs in the first and second steps. The authors recognize this when they say that the calculations can be only tentative,

but the use of the term pilot plant tends to give the impression that the work was done on a larger scale than was actually the case.

The statement is made that all runs were by the batch method but that the method could be made continuous by putting the solution through a number of cells in series. This is obvious, but would it not be necessary also then to put the gas through all the cells in series? If so would not the head and consequent aeration costs be those given multiplied by the number of cells?

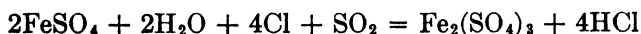
It would appear, also, that a good deal of the work done, and presumably also the cost figures obtained, were on a basis of starting with zero acid and building this up to 5 per cent. It is not practicable in leaching to neutralize the solutions completely; in fact, with the large-scale Inspiration tests there was serious trouble from precipitation of basic salts when the solution acidity was about 2.5 per cent. For the same number of pounds of acid made, twice the volume of solutions would have to be handled for a minimum acidity of 2.5 per cent., compared with a zero acidity; consequently the aeration costs would have to be doubled, if those given in the article were calculated on a basis of original zero acidity.

The percentage of acid needed per cycle in any leaching system is proportional to the copper precipitated; therefore would not aeration costs increase directly as the percentage of copper to be precipitated decreased? Thus, for a weak solution carrying say 0.25 per cent., there would be needed for each cycle say about 0.5 per cent. acid (based on a leaching ore requiring about twice as much acid as copper recovered). It would therefore seem that to make a ton of acid in a 0.5 per cent. solution, the same volume of gas would have to be brought into contact with ten times the volume of solution as compared with making the same amount of acid in a final 5 per cent. solution. In other words, with decreasing necessary acid strength or percentage regenerated each cycle, at some point aeration costs would be prohibitive per pound of acid made. I may have misunderstood the method of figuring used, therefore the above should be taken as a request for information, and not a criticism. However, the cost figures (\$4 to \$10 per ton of actual acid, depending on whether or not roasting and sulfur costs are charged) do not seem to show any particular advantage, except an uncertain possibility of lower installation costs, which need not be considered since amortization is included. With the same conditions of supply of SO_2 , acid can be made for these figures, by the usual methods, per ton of actual acid, but produced at, say, 75 per cent. instead of 5 per cent.

The statement that the process has small operating cost, relatively low first cost, and that it lends itself to comparatively small-scale installations at isolated points is not clear; does this mean a complete leaching process of which the method described is a part, or the method itself? If the former, the fact should be emphasized that there are few possible

small-scale installations at isolated points where money can be made by mining, crushing, leaching with \$10 acid, precipitation with iron at the freight rate to the isolated point, freight out on the cement from the isolated point, together with treatment costs on cement, plus freight, refining, and selling costs on bullion except for much higher than the usual grades of ore. It is, of course, true that there are many small deposits where tonnage would not justify the installation of modern leaching methods, but if the copper from such deposits made by cementation costs more than you can get for it, why bother with it?

W. E. GREENAWALT, Denver, Colo. (written discussion).—Apparently, the first mention in the United States of the conversion of ferrous sulfate to ferric sulfate by means of sulfur dioxide, for leaching purposes, is in a patent to Deby, No. 240309, April 19, 1881, in which is described and claimed, "In the extraction of copper and silver from their sulfide ores, the method consists in subjecting the ferrous sulfate solution to the fumes or gases of sulfurous acid, whereby its conversion into ferric sulfate is effected." Apparently, as an improvement on this patent, another application was filed about a year later by Deby, No. 252593, Jan. 17, 1882, in which is described and claimed "The process of converting ferrous sulfate to ferric sulfate, which consists in subjecting the solution of ferrous sulfate to the combined action of chlorine and sulfurous acid gases." The reaction given is:



Ferric chloride has some advantages over ferric sulfate, but it also has some disadvantages. In the general treatment of the complex ores, containing gold, silver, or lead in connection with the copper, a solution having a chloride basis has a much wider range than one having a sulfate basis.

By the method described in the patent to J. E. Greenawalt, No. 631040, Aug. 15, 1899, in which the leach solution is electrolyzed, and in the patents to W. E. Greenawalt, Nos. 968651, 968845, Aug. 30, 1910, and No. 973776, Oct. 25, 1910, in which is described the application of sulfur dioxide and chlorine to the leach solution, there was no difficulty in getting solutions that would dissolve gold leaf in a few seconds, and when these solutions were applied to the ore, copper, gold, silver, lead, and zinc were dissolved. Certain interesting features, however, developed in the use of these solutions. Both ferric sulfate and ferric chloride solutions quickly disintegrated all diaphragms, even when the highest quality of asbestos cloth was used. Other porous membranes were tried; while some seemed to stand up well when used on a small laboratory scale, when used on a large scale, working continuously day and night for extended periods, no porous membrane was found which had the desired durability. For this reason diaphragms were entirely discarded

in the electrolysis, and mechanical means were developed for aerating the liquids.

It was also found that while acid chloride solutions containing ferric chloride, cupric chloride, hydrochloric and sulfuric acids, and neutral solutions containing also hypochlorites, were effective solvents for the metals in the ores, they also dissolved the lead of the pumps and pipelines. Hard-rubber pumps and hard-rubber pipelines were then substituted but they became soft and buckled with hot solutions, and they became brittle and broke easily with cold solution and repairs were not easily made. These difficulties are not insurmountable, nevertheless, in a commercial plant they would have to be given the most careful consideration.

The electrolytic deposition of copper from mixed chloride and sulfate solutions, like those resulting from the application of sulfur dioxide to a chloride solution as a reducing agent, was not difficult, provided the solutions were maintained reduced. Carbon anodes stood up well. The probable reason for this unexpected result is that chlorides and not sulfates are disassociated by the electric current. The chlorine of the sodium chloride and the metals of the sulfates react to form sodium sulfate and metal chlorides, and sodium sulfate is not readily dissociated under conditions of metal chloride electrolysis.

In the application of sulfur dioxide to leach sulfate solutions, it is interesting to note that the authors obtained an oxidation of the ferrous iron with about the same sulfur-dioxide content of the gas as the writer used in reducing ferric iron in the electrolytic deposition of copper from sulfate solutions. In very complete tests made recently, under small scale working conditions, satisfactory reduction of the ferric iron was obtained with roaster gas that never exceeded 2.0 per cent. sulfur dioxide. Apparently, Deby, as also the authors, oxidized ferrous sulfate to ferric sulfate with a gas similar to that used by Greenawalt in reducing ferric sulfate to ferrous sulfate. The explanation of this is evidently in the nature of the method and apparatus employed. In the Greenawalt reducers, a pool of solution containing ferric sulfate was used and the solution was sprayed into an atmosphere of roaster gas containing not to exceed 2 per cent. sulfur dioxide, by rapidly rotating disks or cylinders having their peripheries only slightly submerged below the surface of the liquid; while in the experiments made by the authors the gas was practically emulsified in the solution. Oxygen is only slightly soluble in water while sulfur dioxide is relatively quite soluble; and, as in the Greenawalt reducers the solution is maintained practically saturated with sulfur dioxide, the oxygen of the pool does not have the same chance to react as when it is all the while being applied to the solution in a finely subdivided or supersaturated condition. The same comparison

would largely apply to the application of the gas in a tower, as suggested by Deby, only not as effectively.

Several years ago comparative tests were made, in the oxidation of ferrous sulfate, between a Pachuca tank and a Greenawalt apparatus of the vertical, mounted, hollow-impeller type from which the gas, delivered into its interior, is ejected into the surrounding liquid in fine bubbles. It was found that the oxidation of the ferrous iron was from four to five times as rapid with the Greenawalt apparatus as with the Pachuca tank.

The development of the treatment of mixed oxide and sulfide low-grade copper ores will be exceedingly interesting. Leaching with an acid ferric-salt solution and leaching and concentration, either by gravity or flotation or both, have their advantages and disadvantages, with the chances probably in favor of leaching and concentration on most ores. Few mixed ores are entirely free from copper in the form of chalcopyrite, bornite, or copper-bearing pyrites, and the copper in these minerals is not readily attacked by any known commercial solvent. Then, too, while the first atom of the copper in chalcocite, Cu_2S , is quite readily attacked by ferric iron, the second atom is not so readily dissolved, and the long time required for the solution of this second atom of copper, to get the desired extraction, will usually bring up leaching difficulties of the first magnitude with most ores, especially where time is an element of the problem, as opposed to heap leaching, where time is not so essential.

G. L. OLDRIGHT (written reply to discussion).—The paper describes a phase of the process developed by the Bureau of Mines for making ferric sulfate and sulfuric acid by means of roaster gas. A general acknowledgment to previous workers was therefore given and for the historical development of the process, readers were referred to a paper by Oliver C. Ralston that is soon to appear. The data obtained on similar work at the Shannon were quite scanty. It is our understanding, however, that the production of ferric sulfate and sulfuric acid by the use of SO_2 at the Shannon property was carried out, on an experimental scale, by Messrs. Rose and Sloan under the direction of Mr. Bennie, prior to Mr. Schimerka's connection with the company. In the brief mention made of the use of oxidizers in lixiviants for other minerals than those of copper, it was not noted that Mr. Van Arsdale has worked with ferric salts on lead as well as copper ores. A much fuller historical account of work on lead ores is given another paper.¹⁴

The authors are familiar with the Hunt and Douglas process and the use of SO_2 as a reducer to precipitate cuprous chloride, and to make acid by the reduction of "ic" salts, but not with the use of SO_2 as an inducer to oxidation. They would like to obtain references of the published

¹⁴ Oliver C. Ralston: Hydrometallurgy of Lead. *Trans.* (1924) 70, 447.

accounts of the simultaneous production of ferric sulfate and sulfuric acid in chloride liquors. Their tests with SO_2 gas on chloride liquors have indicated that iron may be oxidized in dilute, but not in very concentrated brine solutions. Perhaps Mr. Van Arsdale has some additional information.

Information has been requested as to the cost of aeration of very dilute solutions. If the gas analysis, per cent. of SO_2 utilized, and head against which the blower is acting are constant, the amount of power utilized for the aeration itself will be constant per unit of 100 per cent. acid. The extra volume of solution through the cells will have to be paid for by an extra pumping cost, which, however, is not a serious item unless the head is excessive. Were the case otherwise, it would be simple to dilute a stronger acid to the required strength.

A test showing that iron could be oxidized and acid made even in the presence of initial acidity was made to test the possibility of the use of a continuous system, were such deemed feasible. The gas and solution circuits would be entirely separate in this case, the gas being fed to each cell in parallel.

As to the use of the term "pilot plant," complete data as to the size of the plant used and precautions to be observed on increasing the scale of operations were given, so that the use of the term should not be misleading.

With current practice in electrolytic tank houses, the complete precipitation of copper from solutions is accompanied by a very large consumption of power. The electrolytic stripping of discard solutions containing 1 per cent. or less of copper is done only rarely in leaching-plant practice. The Chuquicamata plant has adopted cementation on scrap iron discontinuing electrolytic precipitation.¹⁵ Not only is the power consumption for such a procedure excessive, but the copper precipitated is of very inferior quality.

As to the cost of producing copper by scrap-iron precipitation, Anderson and Cameron¹⁶ say: "The average price paid by the smelter was 12.876 cents per pound . . . the cost per pound, including smelter charges, was 5.815 cents per pound; the operating profit for the period, per pound, was 7.061 cents." From these figures, operations of this nature will support the extra cost of a cent or so for acid, should its use be necessary.

The use of dilute acidic solutions for leaching dumps, capping, and, under favorable conditions, material in place, offers an attractive field for the process that has been described. Acid for these purposes may be advantageously used where (a) the amount of pyrite in semi-oxidized

¹⁵ See C. W. Eichrodt. *Trans. Am. Electrochem. Soc.* (1924).

¹⁶ Recovery of Copper by Leaching, Ohio Copper Co. of Utah. Presented at the Salt Lake City Meeting and issued, as Paper No. 1492-D with MINING AND METALLURGY, September, 1925.

cupriferous material is insufficient to form acid to dissolve the copper present by slow atmospheric weathering, (b) where excessive weathering of the rock limits the length of time an orebody may be leached *in situ* without weathering, (c) where the speed of leaching may be greatly increased, and (d) where it is advisable, on account of scarcity of water, to recirculate the barren solution back over the orebody, and yet there is danger of "plugging" this latter should the iron hydrolyze out.

With present practice, the competition between scrap iron and the electric current as precipitators becomes more keen for ores of such grade that more concentrated copper solutions may be readily made from them. The authors, however, believe that even in this case each of the two precipitation methods will have its own field, and that the statement, "For everything except the very weakest solutions, there is no doubt whatever as to the relative economy of electrolysis as against cementation" is too broad and general.

In the comparative figures for the cost of precipitation by scrap iron and by electrolysis, Mr. Van Arsdale has omitted the extra amortization and interest charges for the electrolytic plant. Many plants, for practical purposes, must be written off during the life of the local orebody and not during the natural life of the material in the plant. Some objection might be made by advocates of scrap iron (scrap turnings and sized scrap from Los Angeles used largely by local lead smelters, cost about \$11 per ton f.o.b. Salt Lake City, the Southwestern freight haul is about the same) that the cost of treatment from local smelters is about \$0.007 instead of \$0.01, and that the difference between cathode and cast copper is about one-eighth of a cent. On the other hand, Mr. Van Arsdale's cost for power seems very conservative. It is, however, almost impossible to list all the factors in one short comparative cost sheet.

The metallurgist may judge for himself what system of precipitation he would have used for the two plants listed below. Unless otherwise noted, the data are from papers on Ajo¹⁷ and the Anaconda leaching plant.¹⁸ As the amount of precious metals in the Anaconda ore was of so little importance that the chloridizing leach was afterward omitted, the two plants should be quite closely comparable. The operation of the Anaconda leaching plant was discontinued on the advent of flotation, as the sulfide ore comprising its feed was readily amenable to treatment by this method.

¹⁷ Ira B. Joralemon: The Ajo Copper Mining District. *Trans.* (1915) 49, 593.
Henry A. Tobelmann and James A. Potter: First Year of Leaching by the New Cornelia Copper Co. *Trans.* (1919) 60, 22.

¹⁸ Frederick Laist and Harold W. Aldrich: The 2000-ton Leaching Plant at Anaconda. *Trans.* (1917) 55, 866.

FACTOR INVOLVED	ANACONDA LEACHING PLANT	AJO
Tons in deposit to be leached.....	20,000,000	12,000,000
Capacity plant, tons per day.....	2,000	5,000
Calculated life of plant, years.....	28	6.6
Copper in ore, per cent.....	0.64	1.5
System precipitation used.....	Scrap iron	Electrolytic
Consumption acid, lb. 60° Bé. (77.7 per cent. H_2SO_4) per ton of ore, using precipitation system above (to judge relative "cleanness" of ore).....	64.9	90.3
Copper in pregnant solution, per cent. (Cycles could be modified).....	1.9	3.0
Cost of acid per ton.....	Assume same operating costs for each company-controlled acid plant; longer haul on acid for Ajo plant.	
Cost of scrap iron.....	Mathewson mentions scrap around plant for Anaconda. For Ajo, Ricketts mentions Alabama pig; Tobelmann and Potter, scrap iron. Cost of scrap iron seemingly somewhat cheaper at Anaconda.	
Estimated cost of power per kw.-hr....	0.535 cents	1.5
	Assuming Mr. Van Arsdale's figure holds for Ajo (probably considerably too high) and adding to maximum Great Falls ¹⁹ power cost of \$25 per horsepower year, assumed \$10 for transmission charges, or \$35 per horsepower year.	
Cost of labor.....	Skilled labor about same, unskilled labor probably cheaper in Arizona.	

The Anaconda plant had a lower grade ore, containing about 30 per cent. less total copper than Ajo, but a smaller plant to amortize, longer estimated life, cleaner ore, much cheaper power, and by cycling differently could have built up a stronger copper solution for electrolytic deposition than 1.9 per cent. Notwithstanding these advantages, the profits were evidently not enough to insure the popularity of electrolytic precipitation. The determination of the exact field to be occupied by each method of precipitation, as stated, is open to judgment of particular cases to a large extent.

It is true that, should the advantages of ferric sulfate be not large for a particular ore, that the Bureau process of making acid, even with scrap iron precipitation assured, would have to compete with acid sold by chamber-acid plants. The cost of making acid is also within the limits of the figures given, as stated. In the cost of acid f.o.b. any locality, however, the cost of freight and profit for the acid plant (unless company owned) enter and \$25 per ton is not an uncommon cost at some treatment plants. The minimum size of ore deposit that may be treated at a

¹⁹ Frederick Laist, F. F. Frick, J. O. Elton, and R. B. Caples: Electrolytic Zinc Plant of Anaconda Copper Mining Co., at Great Falls, Mont. *Trans.* (1920) **64**, 699.

profit should be carefully studied before any process is adopted—we believe there is offered, however, a plant with a low first cost.

Finally, an electrolytic plant is self-supporting in acid only in the rare cases when the ore treated contains enough copper sulfate to balance the acid dissipated by the acid-consuming constituents of the ore. Extraneous acid must then usually be added. The generation of ferric sulfate electrolytically should be credited with whatever voltage drop it may cause by depolarization. It should also be debited with whatever increase in voltage may be required in electrolyzing a colder solution, should this be necessitated by the addition of extra oxidizing agents. Any lowering in current efficiency from the same ferric sulfate that may occur should also be charged, it would seem, to anodic oxidation of ferrous sulfate. The experience at the Chuquicamata plant, at least, has been that both of these latter two charges should be made.

The Conductivity of Electrolytes Used in the Electrolytic Separation of Silver and Gold

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EAST CHICAGO, IND.

(New York Meeting, February, 1926)

THE electrolytic separation of silver and gold has been practiced by the refineries in the United States for a good many years, and probably because of frequent visiting between officials of plants and the consequent exchange of views, operations in the various silver and gold refineries are very similar. We find, for instance, they practically all use electrolytes of approximately the same composition, which, no doubt, is more the result of experience than of studies of electrolytes. At the new electrolytic parting plant of the U. S. S. Lead Refinery, Inc., East Chicago, Ind., considerable attention has been given to the composition of electrolytes, especially to their conductivity and their effect on the character of the silver deposit. We are not aware that anything has been recently published on this subject and are, therefore, presenting such data as we have with the idea that, although it will not be wholly new, it may stimulate interest in the subject.

EFFECT OF COPPER CONTENT ON CONDUCTIVITY

The first work was to determine the specific conductivity of silver nitrate and copper nitrate solutions. Concentrated solutions of silver nitrate and copper nitrate were prepared by dissolving analyzed chemically-pure salts in distilled water, and determining the silver and copper in each. Definite amounts of the concentrated solutions were taken, mixed and diluted to a definite volume. The silver and the copper were determined in each of these solutions and the conductivity was then determined. The plotted results are shown in Figs. 1 and 2. The effect of increasing quantities of silver and copper is readily seen. A comparison of the two sets of curves shows conclusively the benefit of holding the copper content of the electrolyte above 50 g. per liter, as its effect is to increase greatly the conductivity in an approximate propor-

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tion, one unit of copper to one and one-half unit of silver, in electrolytes containing from 30 to 60 g. each of silver and copper.

An electrolyte composition of approximately 60 g. of copper and 60 g. of silver was adopted for the parting plant at East Chicago. This composition proved satisfactory in practice, both as to the conductivity of the electrolyte and the character of the silver crystals. The crystals were heavy and dense and the average voltage drop per cell was approximately 3 volts.

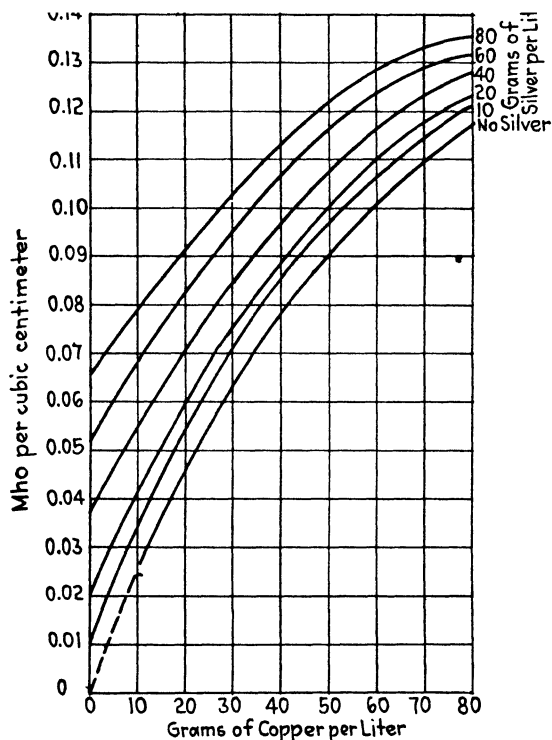


FIG. 1.—SPECIFIC CONDUCTIVITIES OF SILVER NITRATE AND COPPER NITRATE SOLUTIONS AT 25° C. (77° F.).

PRESENCE OF AMMONIA IN ELECTROLYTES

It is commonly known that old electrolytes perform better than new electrolytes, and this was borne out by our experience. At first the character of the deposit varied in different cells, but in the course of time like deposits were obtained. It was then discovered that the electrolyte contained a considerable quantity of ammonium nitrate. Two samples taken after the electrolyte was in use four months showed 19.36 g. and 17.29 g. of ammonia per liter.

The question arose as to why ammonia was present. The usual reactions when copper or silver or silver-copper alloys are dissolved in fairly concentrated warm nitric acid solutions, and the acid is in excess, are:

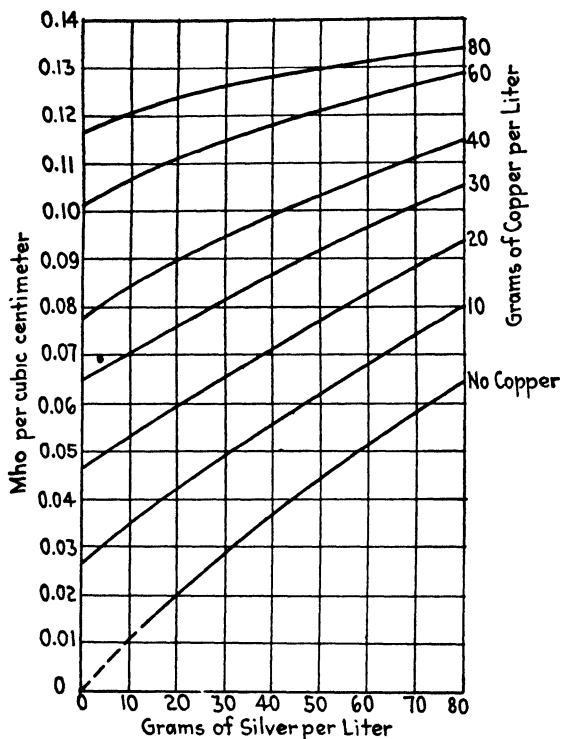
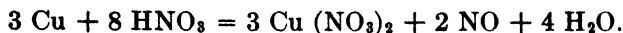
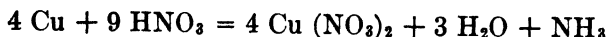


FIG. 2.—SPECIFIC CONDUCTIVITIES OF SILVER NITRATE AND COPPER NITRATE SOLUTIONS AT 25° C. (77° F.).

The reactions, however, are very different if the metals are in excess and the nitric acid solutions are dilute, and not heated; under these latter conditions ammonium nitrate will be one of the products, as shown by the following reactions:



As a rule it is not possible to have reducing conditions with such a strong acid as nitric acid, but when the metal is in great excess, and the acid is comparatively dilute, ammonium nitrate will be produced.¹ The

¹ Reference to this reaction is given in Prescott & Johnson's "Qualitative Chemical Analysis" under Division 6, Reactions A, With Metals, Part III, Nitric Acid.

second set of reactions seemed to explain the presence of ammonia in the electrolyte, as it was the practice to add daily small quantities of nitric acid to the electrolyte.

EFFECT OF AMMONIUM NITRATE ON CONDUCTIVITY OF ELECTROLYTES

It was also noted as the electrolyte became aged that its conductivity increased and the next tests were run to see if ammonium nitrate was the reason thereof. Concentrated silver nitrate and copper nitrate solutions

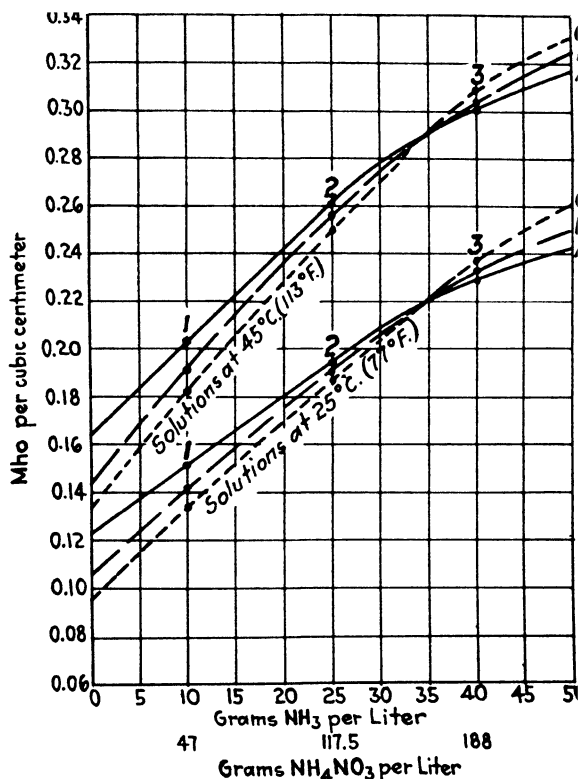


FIG. 3.—SPECIFIC CONDUCTIVITIES OF SILVER AND COPPER NITRATE SOLUTIONS WITH ADDITIONS OF AMMONIUM NITRATE.

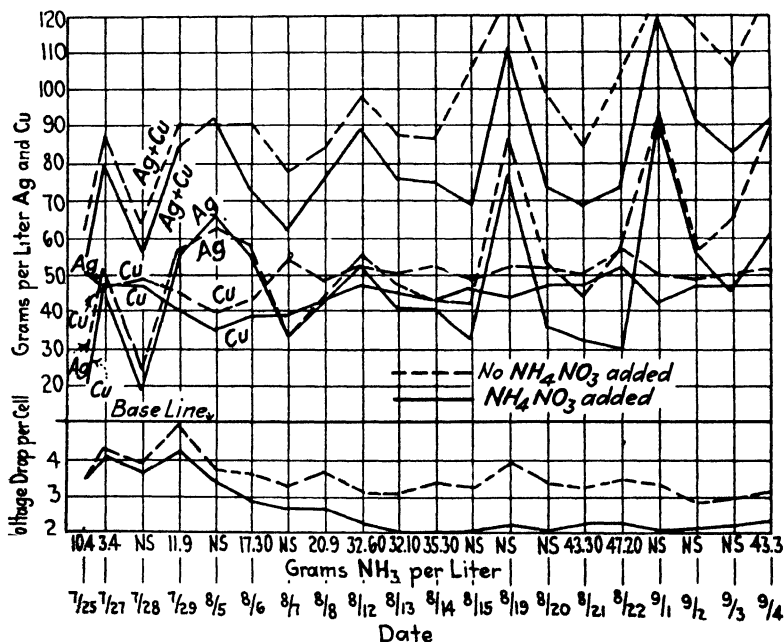
Solution	Grams per Liter				Specific Gravity
	Ag	Cu	NH ₄ NO ₃	NH ₃	
A-0	60	60	0	0	1.218
A-1	60	60	47	10	1.233
A-2	60	60	117.5	25	1.260
A-3	60	60	188	40	1.280
B-0	60	40	0	0	1.172
B-1	60	40	47	10	1.191
B-2	60	40	117.5	25	1.214
B-3	60	40	188	40	1.239
C-0	40	40	0	0	1.145
C-1	40	40	47	10	1.163
C-2	40	40	117.5	25	1.191
C-3	40	40	188	40	1.215

were made up as for the first test, and the ammonium nitrate solution was prepared by dissolving a weighed amount of chemically pure salt in distilled water. Definite amounts of the concentrated solutions were taken and then mixed and diluted to a definite volume. The silver and copper were determined in these solutions, but the ammonia was not, as the dry chemically-pure salt was used. The conductivity of these solutions was then determined. Fig. 3 shows the results.

The results showed conclusively that the presence of ammonium nitrate greatly increases the conductivity of silver-copper nitrate parting-plant electrolyte, and that its effect upon the conductivity is the greatest when the copper and silver content of the electrolyte is the lowest. With 165 g. of ammonium nitrate, equivalent to 35 g. of ammonia per liter, the variation in the silver and copper content does not affect the conductivity as indicated by the crossing of the curves. In this respect, the presence of the ammonium nitrate in silver-parting electrolytes acts similarly to free acid in copper, zinc, lead and tin electrolytes.

Tests on a Commercial Scale

It was then decided to test this effect of ammonium nitrate in regular operations. Two cells were taken and new electrolyte of approximately



4.—CURVES SHOWING VOLTAGE DROP AND COMPOSITION OF ELECTROLYTES USED IN TESTS OF THE EFFECT OF THE PRESENCE OF AMMONIA

the same composition was made for each. These cells were then put into regular operation, and parallel conditions were maintained as nearly as

possible on a commercial scale. The electrolyte in the two cells varied from day to day principally because of the copper in the anodes, but by additions of silver nitrate or copper nitrate they were brought back to approximately the same composition. To one of the cells, ammonium nitrate was added from time to time and the amount of ammonium nitrate present was checked by analysis of the electrolyte for ammonia; the results are shown at the bottom of Fig. 4. NS indicates no sample was taken for NH_3 determination on the dates specified. The temperature and specific gravity of the electrolyte and voltage-drop readings of the cells were taken regularly. The character of the deposit was also recorded. The voltage-drop readings and the composition of the electrolyte were plotted as shown in Fig. 4.

It will be noted in Fig. 4 that the copper content of the electrolyte was maintained fairly constant throughout the test, but that the silver content varied considerably. This variation in silver content was due to the copper content of the dore' anodes and to the operating conditions under which the tests were conducted; but the silver content as well as the copper content as between the two cells was practically the same. The cells are the flat type.

The copper-plus-silver content of the electrolytes shows a gradual increase as the tests proceeded. It will be noted that as the copper-plus-silver content increased, the resistance of the cells was reduced, which is shown particularly by the voltage-drop curve of the cell to which no ammonium nitrate was added. The curve for the cell to which ammonium nitrate was added clearly shows the effect of ammonium nitrate in decreasing the resistance. It also shows that after 35 g. of ammonia per liter were present in the cell, the difference in voltage drop of the two cells was fairly constant. In other words, beyond 35 g. of ammonia per liter, there is no beneficial effect from the ammonium nitrate in so far as conductivity is concerned.

Effect on Character of Silver Crystals

The presence of ammonium nitrate apparently had an effect on the crystalline character of the deposited silver, but not to such an extent as a variation in the amounts of silver nitrate and copper nitrate in the electrolyte. When the silver was below 40 g. per liter the deposit was of a fine crystalline nature; and when the silver content was under 35 g. per liter the crystalline formation was very fine. The effect of ammonium nitrate was to cause the formation of more compact and shorter crystals, and was more apparent as the silver content of the electrolyte was low. At times the crystals tended to form very compactly and to adhere to the cathodes. The results indicated, however, that with high-copper and high-silver content (each above 50 g. per liter), the presence of ammonium

nitrate has a beneficial effect on the character of the silver crystals, causing them to form larger and restraining the formation of long crystals.

Laboratory Tests of Effect on Silver Crystals

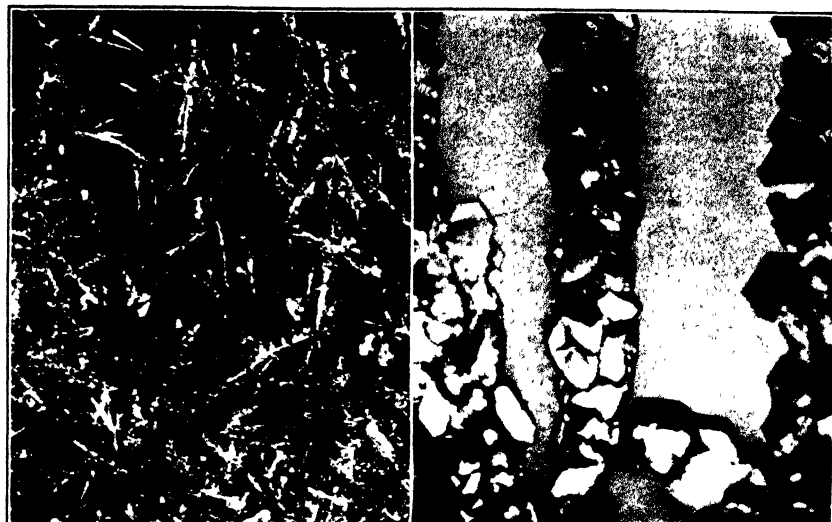
Work was resumed in the laboratory to study further the effect of ammonium nitrate on the character of the crystals, as better control is possible there than in commercial-scale tests. Five electrolytes were prepared by dissolving the pure salts of silver nitrate, copper nitrate, and ammonium nitrate in water and diluting so as to give solutions having the compositions as follows:

Solution	Grams per Liter			Grams Equivalent per Liter			Specific Gravity
	AgNO ₃	Cu(NO ₃) ₂ ·3H ₂ O	NH ₄ NO ₃	Ag	Cu	NH ₃	
I	79			50			1 070
II	79	230		50	60		1 215
III	79	230	83	50	60	17.5	1 248
IV	79	230	165	50	60	35	1 275
V	79	230	215	50	60	45	1 300

TABLE 1.—*Results of the Laboratory Tests*

Period of Test	Voltage Drop between Electrodes, 2.5 In. Apart, Volts					Temperature, ° C.
	Cell I	Cell II	Cell III	Cell IV	Cell V	
Start.....	3.20	1.20	0.80	0.65	0.54	21
4th hr.....	3.19	1.18	0.79	0.64	0.53	24
8th hr.....	3.19	1.18	0.79	0.64	0.53	26
12th hr.....	3.20	1.20	0.82	0.65	0.54	23
16th hr.....	3.19	1.19	0.80	0.64	0.54	25
20th hr.....	3.20	1.21	0.82	0.66	0.56	23
24th hr.....	3.20	1.20	0.80	0.65	0.55	26
28th hr.....	3.25	1.21	0.83	0.67	0.57	23
32nd hr.....	3.22	1.20	0.82	0.66	0.56	26
36th hr.....	Stopped test					
Current efficiency, per cent.....	83	98	98	98	98	
Specific Gravity of Electrolytes						
Cell	I	II	III	IV	V	
Start.....	1.070	1.215	1.248	1.275	1.300	
Finish.....	1.070	1.215	1.245	1.270	1.295	

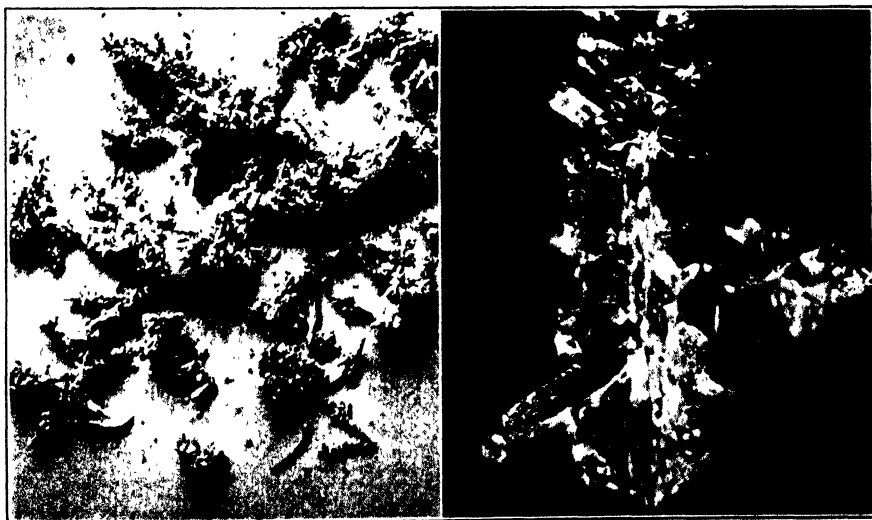
Pure cast-silver anodes and sheet-silver cathodes were used. The latter were coated with a film of oil so as readily to permit the removal of



×2.5.

×60.

FIG. 5.—SILVER CRYSTALS FORMED IN ELECTROLYTE CONTAINING 50 GM. SILVER PER L. ELECTROLYTE I.



×2.5.

×20.

FIG. 6.—SILVER CRYSTALS FORMED IN ELECTROLYTE CONTAINING 50 GM. SILVER AND 60 GM. COPPER PER L. ELECTROLYTE II.

the deposited crystals of silver at periods of about 4 hrs., in the case of all except the deposits formed in solution I., from which the cathode crystals

were removed at about 1-hr. intervals to prevent short circuiting. The anodes and the cathodes were suspended $2\frac{1}{2}$ in. apart in beakers holding 600 cc. of the electrolyte.

The current density selected was 32 amp. per square foot of exposed electrode surfaces, and the temperature of the electrolytes was between 20° and 26° C. The duration of the test was 36 hr. The voltage drop between the electrodes was measured at the start of the 4-hr. periods, after the electrodes were stripped of the deposited silver crystals. Table 1 gives the data.

The difference in the weights of the cathode silver and the loss in weights of the anodes gave the weight of the anode residue as about 0.4

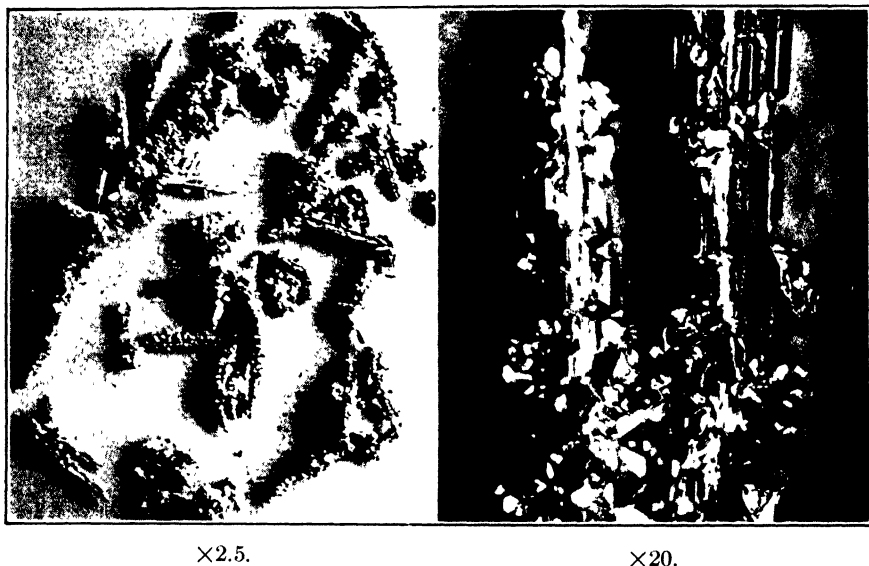


FIG. 7.—SILVER CRYSTALS FORMED IN ELECTROLYTE CONTAINING 50 GM. SILVER, 60 GM. COPPER AND 35 GM. AMMONIA AS NITRATES PER L.; ELECTROLYTE IV.

per cent. in the case of anode I, and about 0.6 per cent. for anodes II, III, IV, and V.

The character of the cathode silver was as follows:

Cell I.—Long slender branching needles, which rapidly grew towards the anode, and unless pushed back to the cathode would short-circuit the electrodes within an hour.

Cell II.—Short thick single and dendritic crystals which formed close to the cathode. An occasional dendrite would slowly grow towards the anode, but in no case caused short circuiting of electrodes in the 4-hr. periods.

Cell III.—Heavier thick crystals than those formed in cell II; the tendency of the crystals was to form compactly.

Cell IV.—Heavier crystals than those formed in cell III. The dendrites which formed on the edges of the cathode, had a tendency to turn back toward the surface of the cathode; the crystals in general were compact and short.

Cell V.—The crystals were similar to those formed in cell IV but in general were more compact and of smaller size; the dendrites on the edges of the cathode formed close to the surface.

The anode residue which formed in cell I was of lighter color than that which remained on the anodes in cells II, III, IV and V; in each test it was removed from the anodes when the electrolyte was stirred.

The character of the silver crystals just mentioned is more clearly shown in the photomicrographs (Figs. 5, 6 and 7).

CONCLUSION

The conclusions deduced from the results of the test conducted in the plant and in the laboratory are as follows:

A. The conductivity of the electrolyte depends upon the silver and the copper content; and the higher the silver and copper content within limits, the greater is the conductivity.

B. Copper in the electrolyte is more effective than silver in increasing the conductivity.

C. The presence of ammonium nitrate materially increases the conductivity of the electrolyte.

D. The effect of ammonium nitrate on the conductivity of the electrolyte reaches a maximum when about 165 g. of ammonium nitrate per liter is present, equivalent to about 35 g. of ammonia.

E. A low-silver and low-copper content of the electrolyte causes the silver to deposit as fine crystals. With very low-silver content the deposited crystals will either be finer or will assume a long slender branching needlelike form.

F. The greater the amount of silver in the electrolyte, up to about 60 g. per liter, the coarser the crystal formation becomes, if copper is present; and with an increase of the copper content, up to 80 g. per liter, the coarser and more compact will be the crystal formation.

G. The presence of ammonium nitrate has a tendency to change the crystalline character of the deposited silver causing it to form more compactly in electrolytes that contain between 40 and 60 g. each of silver and copper per liter.

DISCUSSION

W. BLUM,* Washington, D. C. (written discussion).—This paper is an evidence of the increased interest in recent years in the properties of

* Chemist, U. S. Bureau of Standards. (Discussion submitted through H. W. Gillett.)

solutions used in electrolytic refining. Because of this interest, attention may be called to a few points for future consideration, rather than as a criticism of the present work.

The measurement and recording of conductivities in terms of the actual metal concentrations, lead to the entirely valid conclusion, that for *equal* metal contents, copper nitrate has a much higher conductivity than silver nitrate. It obscures however the far more significant fact that for *equivalent* concentrations, silver nitrate has a higher conductivity than copper nitrate. At first thought it may appear that in refining we are interested in the actual and not the equivalent metal concentrations. Analyses so reported however give no true indication of the changes produced in an electrolyte during electrolysis. If copper and silver both pass into solution from an impure anode, and silver only deposits, the copper replaces part of the silver in the solution, not gram for gram, but in equivalent proportions, i. e. 31.8 gm. Cu for 108 gm. Ag. As a first approximation, therefore (unless free acid is present and is reduced in concentration during electrolysis), the total equivalent content of metal in the solution remains constant. The conductivity data should prove more useful if they represented the change in conductivity when successive portions of the silver, in e. g. $N \text{ AgNO}_3$, are replaced by equivalent amounts of copper. The same considerations may be helpful in connection with the effects of iron and nickel in copper refining baths.

It is generally recognized that formation of ammonia in the electrolysis of nitrate solutions is caused by cathodic reduction. This reaction is the basis of methods for the electrolytic determination of nitric acid. The equations on page 110 therefore probably have no direct relation to this cathodic formation of ammonia, and may even lead to the erroneous conclusion that the ammonia is formed at the anode where the metals pass into solution.

The observation of the authors that the presence of ammonium nitrate caused the formation of finer crystals of silver, might be predicted by the fact that the addition of a common ion (nitrate) reduces the metal ion concentration and increases the cathode polarization.

E. F. KERN (written reply to discussion).—It is obvious "that for *equivalent* concentrations, silver nitrate has a higher conductivity than copper nitrate," but what really concerns the electrolytic refiner is not only to use an electrolyte which possesses high conductivity but at the same time one yielding a satisfactory cathode deposit, which is most desirable. As has been shown by the results reported in the paper, the presence of copper (even though its solution does not possess as high conductivity as silver solution of equivalent concentration) does act *beneficially* in not only causing more desirable silver crystals to form, but it also enables an electrolyte containing a small amount of silver to possess very high conductivity. In reality, these are what most interests

the electrolytic refiner of silver. However, if anyone desires to compare the equivalent conductivities of copper nitrate and silver nitrate solutions, the curves of Figs. 1 and 2 can be immediately utilized without any trouble; for example:

Normality	Gm. per L.	Conductivity Mho per C. C.
3N/4 Ag	81.0 Ag	Approximately 0.065
N/2 Cu	15.9 Cu	Approximately 0.036
N/2 Ag	54.0 Ag	Approximately 0.047
N/4 Cu	8 Cu	Approximately 0.02
N/4 Ag	27 Ag	Approximately 0.028

So anyone familiar with, and who prefers to express concentrations of electrolytes in terms of fractional normalities, can rapidly translate "grams per liter" into "fractional normality" by dividing grams of copper per liter by 31.8, and grams of silver per liter by 108.

It would mean little to the operator of a refining plant to express concentrations of electrolytes in terms of fractional normalities, as from day to day the metal content of electrolytes vary greatly; besides, the metals in the electrolytes are reported by the laboratory as "grams per 100 c. c.," "grams per liter," or "percentage and sp. g. of the solution." It would be far more difficult for the plant operator to figure the metal tie-up in the electrolytes from the fractional normality of the solutions, than for the scientifically trained man to translate "grams per liter" into normality. As a matter of fact, the electrolytic refiner is "interested in the actual, and not in the equivalent metal concentrations." It would be extremely confusing for him to make his reports of the electrolytes as having a stated fractional normality, instead of so many grams per liter. For example: an electrolyte which contains 68 gm. copper and 38 gm. silver per l. has a normality of $2.138 + \text{N. Cu}$, and 0.352 N. Ag . (or $68 \text{ N}/31.8 \text{ N. Cu}$, and $38 \text{ N}/108 \text{ Ag}$). Further: the refiner knows that for each unit of copper which the anodes contain, he must supply to the electrolyte 3.4 units of silver in the form of silver nitrate, which he prepares by chemically dissolving metallic silver, either by adding a calculated amount of nitric acid to the electrolytic tanks, or else by digesting metallic silver in dilute nitric acid and adding the resulting solution to the electrolytic tank. I cannot realize how normality values can aid the refiner.

With respect to the formation of ammonium nitrate in the electrolyte, I believe that it is formed electrolytically by evolved hydrogen at the cathode, and also by the reaction shown by the equation on page 110; the

ammonia which is formed in the cell by direct chemical action is not "formed at the anode where the metals pass into solution" but at the cathode by the free nitric acid added to the cell to form silver nitrate by the dissolving of cathode silver crystals, and by digesting an excess of metallic silver in dilute nitric acid.

F. R. PYNE, Perth Amboy, N. J.—I used sodium nitrate to increase conductivity. The increase was due, in my opinion, to the increased velocity of the sodium ion over that of the copper and silver. We also found that the deposit became quite dense and when we added it in excessive quantities, we had great difficulty in scraping the deposit off the carbon plate. Probably the cause of that is that the nitrate depresses the dissociation of the silver and perhaps gives a more matted deposit.

As the paper states, those who have had experience in electrolytic silver know that the older the electrolyte the better it seems to work.

E. F. KERN.—Mr. Pyne used sodium nitrate a number of years ago at the time that I tried potassium nitrate and practically confirmed the results. I do not know which came first, his or mine. Even with potassium nitrate the effect was to give a finer crystalline form than this exact form. I do not think there would be any great harm in the deposit forming in the plates impregnated with paraffin. The impregnation of the cathode with paraffin does not affect the conductivity of those plates to any great extent.

F. R. PYNE.—In addition to the sodium nitrate I tried at one time adding sulfuric acid which greatly increased the conductivity but the silver came down so dense it almost had to be chiseled off.

S. SKOWRONSKI, Perth Amboy, N. J.—Ammonium nitrate is not necessarily formed in the electrolyte during the refining of silver. With a neutral electrolyte ammonium nitrate will not form. It is the nitric acid which the authors added to the bath which caused the formation of ammonium nitrate. With silver anodes containing tellurium or bismuth as impurities, the addition of nitric acid is not to be recommended as these impurities will become soluble under the acid condition and will contaminate the cathode deposit. For this reason it is the usual custom to add silver nitrate to the electrolyte rather than nitric acid, keeping the silver contents not below 60 gm. per l. The addition of silver nitrate is necessary to keep up the silver content of the electrolyte, due to the fact that other impurities dissolve at the expense of the silver in the anode. For example, for every part of copper present in the anode, three parts of silver will deposit out of the electrolyte, hence if an appreciable amount of copper is present in the anodes the electrolyte will rapidly deplete in silver content.

In the usual process of silver refining the anodic reaction is basic and the slime usually contains from 20 to 25 per cent. of copper present as a

basic nitrate. The cautious addition of nitric acid to the anodic compartment will dissolve this basic nitrate without the introduction of free nitric acid in the electrolyte.

From the point of view of power saving the addition of ammonium nitrate is not essential. Lower voltage, however, gives a better cathode deposit and less chance of contamination of the refined silver with impurities. Under certain conditions with high voltage, even with a neutral electrolyte, some of the palladium present in the anode will dissolve and contaminate the silver deposit.

E. F. KERN.—It may be well to present the method which was used for the determination of the ammonia in the electrolytes, which is rather simple: From 10 to 25 c. c. of the electrolyte, or its equivalent in weight, is placed in an ordinary 250-c. c. distilling apparatus with water-cooled condenser, similar to that used for the determination of arsenic. The solution in the distilling flask is thoroughly neutralized with strong caustic solution and an excess added. The ammonia is distilled and the distillate collected in a 0.3 normal sulfuric acid solution. When large quantities of ammonia are distilled it is important to cool the receiver which contains the 0.3 normal sulfuric acid solution, or have it surrounded by running cold water to assure the entire collection of the ammonia as it is distilled over. After the distillation is complete, the excess sulfuric acid is titrated with 0.3 normal caustic solution, and the ammonia calculated from the amount of sulfuric acid which it neutralized. Results by this method were checked in the plant laboratory and by Mr. Chapman of the Indiana Laboratories, Hamond, Ind., on synthetic solutions, which were made by adding ammonium nitrate to some of the electrolyte. The results of the check determinations checked exceedingly close, showing that the method gives good results. A preliminary distillation and titration are sometimes run, in order to determine the approximate amount of 0.3 normal sulfuric acid solution necessary to collect the distillate.

H. H. ALEXANDER, Westfield, N. J.—Dr. Kern's statement covering the amount of copper in the electrolyte is very important. When we first started the electrolysis of silver, it was considered advisable to keep the copper in the electrolytes low—as I recall, not over 15 or 20 gm. Holding the amount of copper to such a low figure required the removal of too much solution, and it was allowed to build up in the electrolyte. We found when the copper content were between 60 and 70 gm., better results were obtained.

E. E. DIEFFENBACH, Newark, N. J.—In the Balbach plant we never looked for ammonia in our solutions. While our deposit of silver almost always came in large crystals, it never came in such large crystals as Prof. Kern shows in the bottles. It is well known that copper helps the

deposition of silver. A little copper in solution will give a nice gold deposit on the cathode.

E. F. KERN.—In doré there is considerable selenium, but by adding nitric acid to the cell direct there is no trouble in any way.

S. SKOWRONSKI.—In the reduction of the slime in the cupel or doré furnaces, the selenium is far more easily removed than the tellurium, and with a slime assaying high in tellurium a small amount of tellurium remains with the doré silver, whereas selenium is seldom if ever found in this metal.

E. E. DIEFFENBACH.—If you do not get doré free of selenium, the deposit of silver in the tank of copper is like a black mud. In other words, it does not deposit nice, gray, metallic, bluish crystals. You have to take it out in baskets. To make a good sulfuric acid parting, you must get rid of selenium.

E. L. JORGENSEN, Irvington, N. J.—My experience has been similar. By boiling a little longer the selenium can be driven out. There will be a red deposit of selenium in sulfuric acid parting, and you will be able to get the clean-cement silver just the same.

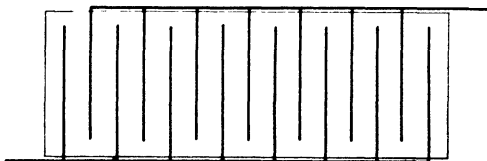
Improvements in the Series System of Electrolytic Copper Refining Recently Developed by the Nichols Copper Co.

BY M. H. MERRISS*, NEW YORK, N. Y.

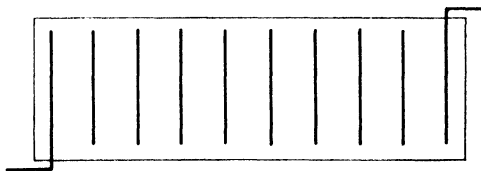
(New York Meeting, February, 1926)

IN THE last few years, there have been developed at the plant of the Nichols Copper Co., Laurel Hill, Borough of Queens, New York City, improvements in electrolytic copper refining by the series system that have materially increased the flexibility and economy of that system. The purpose of this paper is to discuss, as of interest to refiners and to those who have copper to refine, as well as to the engineering profession in general, the changes that have taken place resulting in wider application and increased efficiency of the series system.

Copper is electrolytically refined in two ways, which are spoken of as the "multiple system" and the "series system." In both systems, the electrolytic tanks are in series electrically. In the multiple system the electrodes in a single tank are in multiple or in parallel, thus:



In the series system, the electrodes in a single tank are in series, thus:



There are two important adaptations of the series process, one represented by the series electrolytic tank room at the Baltimore Copper, Smelting & Rolling Co., Baltimore, Md., and the other by that of the Nichols Copper Co.'s plant. At Baltimore, the anode is rolled to perfect

* Assistant to the Vice-president, Nichols Copper Co.

smoothness and uniform thickness, cut into small rectangular pieces, framed with grooved wooden strips and supported in the tanks with a wooden frame, which also determines with precision the distance between anodes. The dimensions of the finished framed anode are 22 by $24\frac{1}{4}$ by $\frac{5}{16}$ in.,¹ therefore its weight is comparatively low and the tanks comparatively small. The tanks are loaded and unloaded by hand, the anode being of a convenient size for this purpose; there are no cranes in the tank room, and this adaptation of the series system does not lend itself, as far as the tank room is concerned, to mechanization.

Quite different is the "Nichols series" process, as it may be conveniently called for the sake of brevity, and it is this adaptation of the series system that it is the purpose of this paper to discuss. The anodes are much larger, being about 54 by 12 by $\frac{3}{8}$ in. They are cast upon a circular casting machine and are sufficiently smooth and uniform in thickness, so there is no necessity of rolling. They are hung in tanks by means of cranes and are removed in the same way. More details of the process are given later. Having thus briefly outlined the essential difference between the multiple and series systems and having stated the outstanding divergencies between the two present adaptations of the series system, it may be of interest to give a summary of the historical development of electrolytic copper refining, with special reference to the kind of installation chosen in each case.

HISTORICAL

The original electrolytic copper refinery in the United States was that of the Balbach Smelting & Refining Co., which, about 1883, installed a small multiple system patterned along the lines of refineries in operation at that time in Germany. Some time thereafter small multiple plants were erected at Baltimore, Md., at Pawtucket, R. I., and in Montana. About 1890, Hayden developed his process in Bridgeport and shortly thereafter was engaged to install it at the Baltimore plant. The Baltimore series plant started operation in the fall of 1891. About 1892, the Nichols Copper Co. started a small refinery using its present system. About 1895, a multiple plant was erected at Maurer, N. J., somewhat similar to the Balbach one, but with trolleys for handling copper into and out of the tanks. That a multiple installation was chosen seems to have been due largely to the fact that the copper to be treated was very impure and high in silver. Individual busbars were used on the sides of each tank, so that the copper tie-up in busbars per pound of copper output was high. A few years later (1902) Arthur L. Walker developed his "multiple-series" tank room; by placing a number of tanks side by

¹ H. O. Hofman and Carle R. Hayward: "Metallurgy of Copper," 396. McGraw-Hill Book Co., New York, N. Y., 1924.

side he eliminated the heavy copper busbar, except on the end tanks, substituting a small bar of triangular section between the intermediate tanks. This arrangement materially reduced the amount of copper required for busbars and also decreased the loss of voltage between tanks. Professor Walker's idea was so successful that the tank room of the Raritan Copper Works, which had been built meanwhile along the old lines, was remodeled, using the small triangular distributing bars. Coincident with the introduction of the Walker method, traveling cranes were introduced; but, up to this time and for many years thereafter, all the tank room operations in both series systems were by hand, there being no crane work of any sort.

Shortly after this, when refineries were erected at Chrome and Tacoma, it was natural to put in the multiple system inasmuch as considerable study had been devoted by copper refining metallurgists to the proper construction, mechanicalization and operation of multiple tank rooms, resulting in material improvements in them. On the other hand, no new series plants had been erected, it being generally understood that the series system was comparatively underdeveloped. Furthermore, it was believed that the multiple system was much more flexible and applicable to a much greater variety of coppers than the series system, especially coppers containing high antimony, high lead, and high silver. This was largely due to the fact that it had been found impossible, at Baltimore, to roll an anode satisfactorily unless it was very pure. Somewhat similar considerations doubtless influenced the erection of the Baltimore multiple refinery and the new Great Falls refinery, reenforced by the additional argument of the increased rates for labor at that time, which precluded the use of a tank room without labor-saving devices. The interchange of ideas between large numbers of engineers engaged in constructing and operating these multiple plants resulted in developing the multiple system intensively, as well as giving these developments wide publicity. This created the impression that the refining art, as practiced by those using the series system, was standing comparatively still, or at least that its progress was much slower, it being generally recognized that refiners operating series installations kept more to themselves. The point to be stressed is that for various reasons—some of which have been indicated above—the series system did not receive the same intensive and constructive study by the engineering fraternity as a whole as had been applied to the multiple system.

At the same time, due to original excellence of design and to fundamental advantages of its system, the Laurel Hill plant, guided carefully by such men as Dr. W. H. Nichols, Dr. J. B. F. Herreshoff, J. B. Herreshoff, Jr., and W. C. Ferguson, maintained its competitive position, producing (for many years on the largest scale of any refinery) electrolytic

copper of such high grade as quickly to attain a reputation for unexcelled quality, which has ever since been maintained.

THE NICHOLS SYSTEM

A general outline of the copper refinery of the Nichols Copper Co. at Laurel Hill, Long Island, has been published elsewhere.² Stripped to its essential metallurgical steps, and without reference to dimensions or methods of handling, the Nichols series system is as follows:

A smooth anode of uniform thinness is cast, and five of these are suspended from an iron hanger bar, making a "row." These rows are

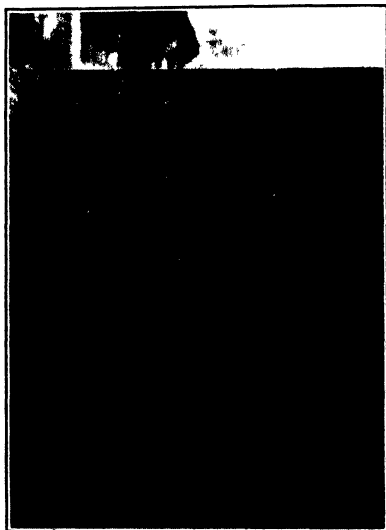


FIG. 1.—SUSPENSION OF ANODE UNITS IN MASTIC-LINED TANKS.

accurately spaced in tanks much deeper and wider and somewhat larger than other copper refining tanks (see Fig. 1). At a given period, the spacing may be such that about 100 to 125 rows are placed in a tank. Current is introduced at one end of the tank and travels from row to row through the electrolyte, dissolving copper from one side of each row and depositing it upon the adjacent side of the next row. In other words, each tank is really from 100 to 125 depositing "cells," or electrolytic units. Starting sheets, as used in the multiple system, are eliminated; spacing can therefore be much closer; and large yields are obtained per unit of power and per square foot of tank area, building area, and land. There are no double or triple pullings of cathodes per anode, and no multiplicity of contacts to be kept clean. Both of these facts result in a considerable reduction in number of men employed.

² The Smelter and Refinery of the Nichols Copper Co. *Eng. & Min. Jnl. Pr* (1925) 119, 290.

When all but 8 to 10 per cent. of the anode has been converted into cathode, the electrodes are removed from the tank and the remainder of the anode is stripped off. The "backs," or anode remains, return to the anode furnaces, while the cathodes, long and narrow, are charged down chutes into melting furnaces preparatory to molding into wirebars and other merchant shapes. The shape and thinness of the cathodes are ideally adapted to such a method of charging, which saves time, labor, and furnace repairs, as well as altogether eliminating charging machines, and admission of unnecessary false air.

Anode Department

The anode is long, narrow, cast by hand, and delivered to the "assembly" or "preparation" department in piles on small industrial cars. The furnaces are efficient but not large. The anode is intensively refined in these furnaces, its "set" being very nearly equal to that of wire-bar copper. Its copper content is at least 99.20 per cent. and often runs up to 99.60 per cent. It is certainly the best anode produced today from a physical standpoint, being absolutely free from blisters, fins, splashes, or edges of any kind, and extremely uniform in thickness. In spite of these facts the cost of its production is only slightly in excess of the cost of producing multiple anodes, whereas the expense of rolling (deemed necessary in the other series process) is entirely eliminated.

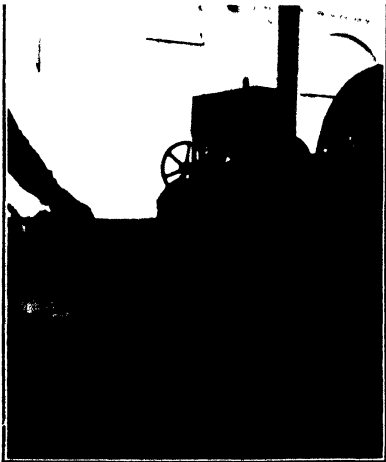


FIG. 2.—MACHINE FOR PUNCHING LUGS IN ANODES.



FIG. 3.—RACK CARS FOR ASSEMBLED ANODE UNITS.

Assembly or Preparation

Up to very recent years, each anode was taken from its pile on the industrial cars, straightened, punched, brushed to remove loosely adhering scale, painted, and returned to a similar pile on an industrial car, all

by hand, and then pushed into the tank room. This meant 100 per cent. hand labor, involving the repeated liftings, handling, turning over, etc., of a 90-lb. piece of copper. This procedure has been supplanted by the largely mechanized operation depicted in Figs. 2, 3 and 4.

The anode is now taken from its pile; straightened, if necessary, by a couple of taps with a hammer; punched; and pushed on to a set of conveyor rolls pitched at just the right angle to carry it down to a set of horizontal rolls wide enough to receive five anodes. These rolls consti-

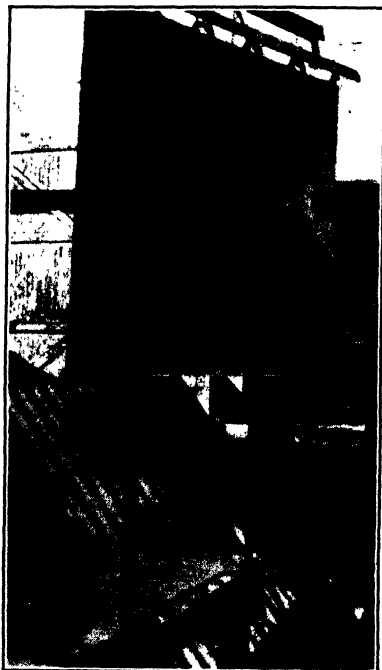


FIG. 4.—TILTING TABLE FOR ANODE ASSEMBLY.

tute a tipping table, which can be turned to a vertical position at the will of an operator, who stands at its head attaching the unit of five anodes to an iron hanger bar by means of ten copper rings. From the vertical position, the unit is lifted by an air hoist and set in a rack car, where it is sprayed on the set side with a resinous soap emulsion. The rack cars, each representing one-sixth of a tank, are pulled in long trains to their destination in the tank room by storage-battery locomotives.

The object of the resinous spraying (or "painting," as it is called) is to facilitate the subsequent stripping of the remains, or "backs," of the anode from the deposited cathode. Much work has recently been done in the determination of the exact temperature of anode at which it is best to paint, resulting in greater ease of stripping. The paint itself

has been the subject of careful study, with the result that its composition as well as its manner of application have been simplified and cheapened, with an actual betterment in stripping conditions.

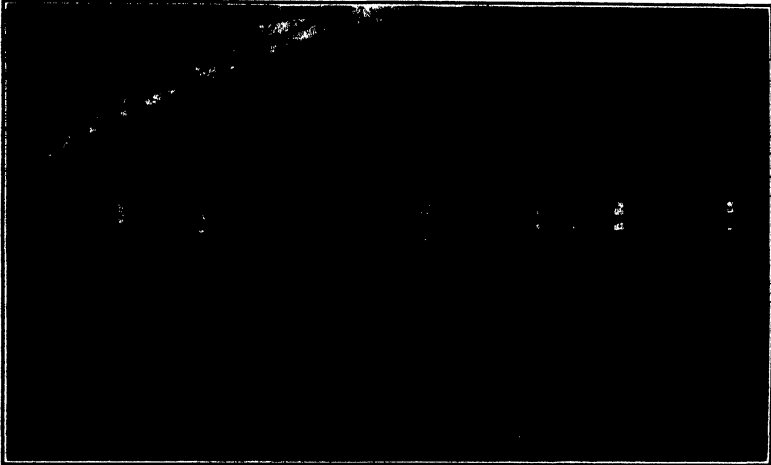


FIG. 5.—NEW TANK ROOM WITH ENLARGED CONCRETE TANKS LOADED AND UNLOADED WITH CRANES.



FIG. 6.—CRANELESS TANK ROOM AND WOODEN TANKS.

Tank Room

When the piles of painted anodes had been pushed into the tank room and into position alongside of the tanks, they were formerly hoisted by hand over the sides of the empty tanks, received by a man standing down in the tank, and hung individually from the iron bars. As the tanks

are about 5 ft. deep the arduous nature of the labor required can well be appreciated. When the tanks were to be unloaded, the process was reversed. With the thinner anode formerly used and with low labor rates, these hand operations were economical but the labor scarcity and higher wages of the war period led to the installation of cranes. Figures 5 and 6 illustrate the difference between the old "craneless" tank room and the present mechanized operations. The cranes have been

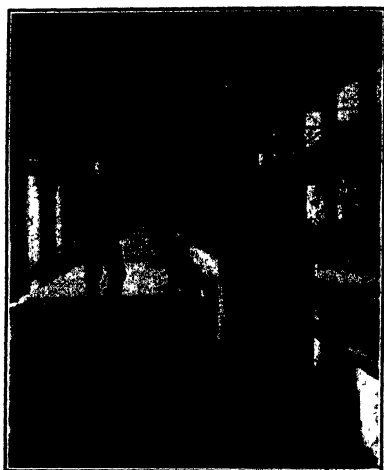


FIG. 7.—CRANE HOISTING ASSEMBLED ANODES.

installed in the tank-room building just as it originally stood, with transfer bays so that a single crane can serve many bays. The rack cars are now run in on tracks between the tanks, and the crane, by means of a lifting frame, hoists one-sixth of a tank of anodes and charges them into the tanks (see Fig. 7). The same procedure is followed in unloading the tanks. As a result there have been important labor savings. Further mechanization in general tank-room layout is contemplated.

Concrete Tanks

Perhaps the most important single development in the Nichols process has been the design and installation by the staff at Laurel Hill of a reenforced-concrete tank to replace the wooden tanks formerly used. In both cases, the actual tank lining is an asphalt mastic, which both insulates the tank from electric current and protects it from corrosion by the tank-room electrolyte running high in sulfuric acid. The wooden tanks lasted about 7 years, when loaded by hand. The oldest concrete tank was built about 1913-14 and is still in good condition; others, now from 3 to 5 years old, have never shown leakage. It is believed that, as long as the proper attention is given to the composition and installation of the mastic lining and to keeping this lining in good condition by regular

attention, the concrete tanks will have an indefinite life. In addition, the reenforced-concrete construction of the tank makes it much more rigid than a wooden tank. This is of importance now that tank loading and unloading is by means of cranes, involving considerable stress on the sides of the tanks when anodes are lowered into place. At the same time, the concrete tanks have been lengthened, making them more than double the size of the wooden tanks, resulting in circulation and labor economies, as well as cheapening tank repairs. The temperature of the electrolyte varies from about 122° to 132° F. in the "receivers," or heating reservoirs, and from about 117° to 125° in the mastic-lined tanks. At these temperatures, the mastic lining used, which is a blend of asphalt and blown oils, has remained hard and unattacked. Elimination of lead tank linings saves not only the capital necessary for such a large lead tie-up, but more especially the heavy lead-burning tank repair costs common in other refinery practice.

Power Consumption

Much has been said about the relative power consumption in the series and multiple systems of refining copper. The facts with respect to the Nichols series process are best shown by the following figures, representing actual operating results of five successive years at Laurel Hill:

CURRENT DENSITY, AMP. PER SQ. FT.	COPPER DEPOSITED, LB. PER KW.-DAY
18.3	307
17.0	345
17.1	373
17.4	354
19.5	328
Average, 17.9	341

These figures indicate the remarkably low power costs that can be obtained with a properly operated series tank room. In multiple practice, 200 lb. per kw.-day would be considered excellent. These results do not represent any single tank or any special portion of the refinery but show the actual final result for the entire electrolytic plant for the whole year. Furthermore, they are based on voltages and ampere readings at the power-house switchboard and, therefore, include all busbars, line losses, and contact losses. The reasons for the power saving are simple and may be briefly stated as:

1. Narrower spacing, made possible by a more carefully cast and more carefully refined anode, and by the elimination of the thin starting sheet with its tendency to bend easily and short circuit.

2. Elimination of all the electrical connections necessary in the multiple system, such as busbar to anode, cathode to starting loop, starting loop to hanger bar, hanger bar to busbar.

There is also eliminated what might be termed "line loss," represented by the small but cumulative losses as the current travels through the anode lug, cathode loops, hanger bars, and the intermediate busbars in the multiple system. All the suspending apparatus in the series system is simply for the purpose of hanging the electrodes and serves no additional electrolytic purpose, as is the case in the multiple. The current is simply introduced at the end of the series tank; from that moment until it leaves at the other end no part of it is consumed in overcoming contact resistances.

It is to be realized that the ampere efficiency of the series system does not get much above 70 per cent., being low on account of leakage through the electrolyte above, below, and around the electrodes. The "power" efficiency, however, to coin a phrase for "pounds per kilowatt-day," is consistently high under properly controlled working conditions.

Original Cost

The original cost for building a Nichols series tank room would be considerably less than that for building a multiple one, given identical conditions and capacities. The criterion usually relied on is the "square feet of tank-room area required per ton of cathode copper deposited per day." At Laurel Hill well under 200 sq. ft. of tank room is required per ton per day. The best claim for the multiple system that has been published recently is 330.³ These figures include the necessary space for working aisles, pumps, receiving tanks, heating tanks, stripping space, etc., and the receiving and filtering of slimes, but not for further slime treatment. About two-fifths of the multiple tank room cost could, therefore, probably be saved, and without any offsetting increase of importance elsewhere in the refining process.

Busbars

Normally, series-system power is transmitted from power house to tank room at about 225 to 240 volts, through very small busbars carrying only about 1000 amp. Multiple-current normal voltage is around 110 to 130. For a 25,000,000 lb. monthly capacity, a multiple plant running at 10,000 amp., with 90 per cent. ampere efficiency, would require about 1475 tanks and would probably have three circuits of 10,000 amp. each. A series plant of the Nichols type would require, at 500 amp. and even as low as 65 per cent. ampere efficiency, only about 340 tanks and would consist, electrically, of ten 1000 amp. "systems" each subdivided in turn into two 500 amp. "legs," or divisions, of about seventeen tanks each. Figures based on the above premises reveal that the weight of busbar used in the series condition described would be roughly only

³ H. O. Hofman and Carle R. Hayward: "Metallurgy of Copper," 402.

one-quarter of that in the multiple, even using intermediate small triangular bars between all possible multiple tanks. (Two cascaded sections, seventeen tanks to a cascade, thirty-four to a section, were used in the estimate.)

The Nichols series system does away entirely with copper hanger bars (except one at each end of each tank), copper loops, copper starting blanks, and stock of copper starting sheets, the total of which amounts to a considerable interest item in a refinery of the above size. Added to this is the fact that the amount of electrolyte used is not over 60 per cent. of that used in the multiple for the same output.

Power-house Installation

The low power consumption in the series system naturally has a marked effect on the overall cost of power-house installation necessary for such a refinery. Assuming a multiple deposit of 200 lb. per kw.-day as compared with the above average of 341 lb. per kw.-day, there necessarily must be provided about 70 per cent. more power-house generating and converting capacity.

Apart from this, however, there is an advantage in a series installation which reputable manufacturers of this type of equipment estimate to be in the ratio of 1 to 1.13. This is chiefly due to the fact that the product of the conversion will be a current of from 8000 to 12,000 amp. at about 125 volts in the case of the multiple and but 1000 to 2000 amp. in the series at about 250 volts.

As shown above, three 10,000 amp. machines would be required for the multiple and, say, five 2000-amp. machines for the series. Inasmuch as copper required varies as the square of the relative amperage, theoretically, about nine times as much copper would have to be built into the generative and converting apparatus for a multiple unit as for a series unit.

Silver and Gold Loss

The question of silver and gold losses in the series system is an interesting one. The actual operating results at Laurel Hill for the five years previously referred to are:

SILVER CONTENT			GOLD CONTENT			
OUNCES PER TON		PER CENT. LOSS	OUNCES PER TON		PER CENT. LOSS	
ANODES	CATHODES		ANODES	CATHODES		
36.8	0.83	2.2	0.53	0.009	1.7	
35.0	0.79	2.3	0.59	0.011	1.9	
27.0	0.68	2.5	0.52	0.010	1.9	
25.0	0.58	2.3	0.54	0.011	2.0	
24.4	0.62	2.6	0.71	0.016	2.2	
Average.....	29.6	0.70	2.4	0.58	0.011	2.0

Assuming that in a multiple refinery with anodes averaging as above, the cathode silver analysis were 0.25 oz. and the cathode gold analysis were 0.005 oz., the balance against the series system would be only about 40 cents per ton of copper refined. Furthermore, individual results obtained from time to time have proved conclusively that the percentage loss of precious metals would decrease materially with an increase in precious metal content of the anodes.

Impure Blister Can Be Used

For many years it was believed that only the purest of blisters could be used in the series system. There were two reasons for this belief:

1. At Baltimore, the introduction of a comparatively small amount of certain impurities renders the copper incapable of satisfactory rolling.⁴ It was therefore impossible for that plant to treat many kinds of blister coppers. A multiple unit was accordingly built, and the combination of one multiple and one series unit gives the flexibility desired. The above situation created an impression in the minds of many that Laurel Hill was limited in the same way. Inasmuch as no rolling is necessary, such an impression is entirely erroneous so far as Nichols is concerned.

2. So much pure copper was formerly received at Laurel Hill that there was no need for flexibility or development of the series process there to make it applicable to more impure blisters.

It can now be given as the opinion of the Nichols staff of engineers that any anode can be treated by their process whose solution in the electrolytic bath will proceed fairly uniformly. This widens the field of blisters to which the Nichols series system is applicable, to include all the large productions of the modern copper mines of the world, at present purities. This allows for the fact that the pure blisters would be mixed with the impure, as is the case in every refinery.

As a matter of fact, considering the six large refineries of the United States, at least two are at present receiving much purer blister than Laurel Hill. The intake of blister at the Laurel Hill refinery is probably the lowest of any in copper content, its total impurity content probably the highest but one, and the total amount of each individual impurity probably not the lowest in any single case.

The flexibility for the Nichols series process has been achieved mainly by varying the electrode spacing and by controlling the smoothness of the cathode deposit by the treatment of the electrolyte with suitable addition agents. Whereas for some time an unchanged spacing of electrodes had been adhered to, it has been found that for blisters of differing grades cheaper overall refining costs are obtained by altering this as much as 15 per cent. In general, wider spacing permits the use of more impure blister; while for purer material, the spacing is narrowed. The desired

⁴ H. O. Hofman and Carle R. Hayward: "Metallurgy of Copper," 399.

flexibility is thus obtained and the spacing chosen, over a period, for blister of given intake analysis represents a nice adjustment between costs for power, labor, and "back" remelting, ampere efficiency, and refinery capacity.

Treatment of Electrolyte

Unlike multiple practice, it was formerly believed unnecessary to add glue to the electrolyte at Laurel Hill, though small amounts of chlorine were used. As long as the anodes were of extremely high purity, this practice was correct. With a desire to treat blisters of widely differing and sometimes variable content, however, came the necessity for glue additions to preserve smooth, close-grained cathode deposits, and a great deal of work was done, first on a one-tank scale, then on a one-circulation scale, and finally throughout the whole tank room, with excellent results.

It was found necessary and desirable to use chlorine (added as common salt) a little more freely, carrying perhaps twice the content formerly thought best; and also to introduce glue and oil for their respective purposes of making deposited copper smooth and tough.

Arsenic content of electrolyte was increased fourfold without deleterious effects, while antimony content is now as high as in multiple practice. Contrary to what was formerly the opinion of those interested in copper refining, it is believed that the limits of electrolyte impurities in the series system are about the same as those in the multiple system.

The effect of varying copper and acid content was carefully observed and most favorable results were found to be obtained when free sulfuric acid was kept between 16 and 17½ per cent., copper content between 2.60 and 2.85 per cent., and chlorine between 0.00035 and 0.00060 per cent. More especially, however, adequate precautions of all kinds were taken to insure the maintenance throughout the whole 24-hr. period of absolutely constant electrolyte conditions in every respect. Segregation of all sorts was minimized, all additions and alterations made as gradually as possible, and individual tank circulations, which are low at Laurel Hill (3 to 5 gal. per min. for a tank 16 by 5½ by 5½ ft.), kept perfectly uniform. After all, probably the most vital single factor in tank-room operations everywhere is, having established a set of conditions that produce smooth deposits, to minimize in every possible way any variation in each of the many conditions in the set.

The action of a solution of glue added uniformly to an electrolyte has long been known to have the effect of smoothing or maintaining smooth a growing cathode deposit. It is believed that this effect is more a physical than a chemical one. The very dilute glue solution is introduced in as continuous a manner as possible, so that a gelatinous film will uniformly cover the projecting points much as snow falls upon a rocky promontory.

A plausible theory is, that the film being of relatively high insulating tendency, the nodule is shielded from negative discharge, and the backward parts of the cathode surface instead are built forward, constantly tending to level up the depositing surface.

The amount of glue to be added, then, is that amount found necessary to provide a film of sufficient thickness or resistance to bring about the end sought. It is possible to use a smaller quantity, which forms a film semipermeable by the current, giving an intermediate control, provided, however, the chlorine content be kept lower. In other words, the most dense cathode is made by a careful regulation of the chlorine content so as to be crystal forming; and then just counteracting this effect, which readily accelerates, by the masking effect of a glue solution of proper concentration. To do this adequately, and yet not in excess, at Laurel Hill has been found to require approximately 1 oz. of glue per hour (in the concentration of a 0.6 per cent. solution) per million pounds of electrolyte.

It is believed that the use of the customary grade of glue does not raise the ohmic resistance of the electrolyte materially, if any at all, but that the well-known increase in power consumption through its use is due to the additional voltage required to force current through the gelatinous film.

Additional Improvements

These excellent results have been furthered by other improvements, smaller it is true but none the less important, as can be appreciated by those who realize the attention to minute detail necessary to keep a tank room at the very top notch of efficiency. Chief among these are the following:

1. A special flat-bulb light has been designed, which can be inserted between even as narrow spacing as that used at Laurel Hill. After the anodes are hung, every row is examined most carefully by the illumination of this lamp, and adjustments made as to plumbness, uniformity of spacing, etc. With this minute inspection possible, it is rarely necessary to lift any electrode out of the tank during its run. Quite the opposite is the case in ordinary multiple practice, where the thin starting sheet, no matter how carefully adjusted, may warp under some systems of operation as soon as the hot electrolyte strikes it. Furthermore, there are two, three, or even four starting sheets to one anode. Gangs of inspectors, "hot sheetmen" and "sheet-straighteners" are kept busy. At Nichols, the only inspection is by reading voltages across the ends of the tanks once or twice each day. Should the voltage go below normal the trouble is located, otherwise the tank is left alone.

2. Special recording thermometers and recording steam-pressure gages were installed for the purpose of keeping an absolute check on

electrolyte temperatures at all hours and upon reasons for any irregularities in them. More adequate heating apparatus was also provided. The result has been more uniform electrolyte conditions, which, as stated above, are the foundation of success in maintaining smooth deposits at Laurel Hill.

3. The filters and settling tanks for removing suspended slime and float have recently been entirely redesigned and rebuilt in order to clarify the electrolyte better, another step in the direction of assuring better electrolyte conditions.

Stripping

Formerly, the electrodes unloaded by hand from the finished tanks were piled flat upon small industrial cars and pushed by hand into the stripping room. Here each electrode was thrown to the ground and stripped, the "back" and cathode being later reloaded on to other cars. Part of the mechanization of this step of the process has been completed. The electrodes are now unloaded by cranes on to rack cars, which are pushed, in train lots, into the stripping room with storage-battery locomotives. The room itself has been enlarged and a $7\frac{1}{2}$ ton Bedford crane installed. This picks up the carloads of electrodes and carefully lets them down to the ground, so that they lie flat, "backs" up, like a partly spread out pack of cards. In this position the hanger bars and suspension rings are easily disengaged. The men then take off the "backs" and toss them to one side and immediately load the cathodes on waiting cars. Separate carloads of backs and cathodes are then pushed to the scale by tractor.

It is confidently expected that a machine will be designed for the stripping operation. Even as it is now performed, it is not unreasonably costly. It is safe to say that this cost is more than balanced, in the multiple system, by the cost of producing starting sheets, looping and hanging them, and straightening them after a 24-, 36-, or 48-hr. deposit upon them. All of these steps the series system eliminates.

Quite a little work has been done, with considerable promise of ultimate success, along another line, which has in view the same objective of reduced stripping costs. Instead of calling a tank finished when the backs are found to be down to 8 per cent. it is proposed to allow the current to continue. Some "redeposition" will set in, but the percentage of backs will decrease. Theoretically, if carried far enough, there will eventually be no backs to strip (the anode lugs would be knocked off or sheared off); the penalty would be increased power costs. Practically, there is a point at which a large percentage of cathodes will require no stripping, the power cost will not be unduly increased, and the balance of the electrodes will fall naturally into two classes: (a) with small percentage of back to be stripped, and (b) with large enough percentage of

back to pay to send to special "hospital tanks," provided to deposit all the "backs" off such transient "cathodes" in a two- or three-day period.

The first difficulty that was encountered in these experiments was that when the anode back was entirely dissolved off, the cathode, having nothing to hold it to the suspending anode lug, fell down into the tank. This has been overcome by the installation of overflow-height regulating devices, which enable the tank-room operators to regulate to a nicety the depth to which the electrodes are submerged, and to vary this throughout the life of the tank through a range of $\frac{3}{4}$ in., thus controlling speed of anode solution up near the lug. When the anode is entirely dissolved, there is now no sharp line at which the lug will break off, but a $\frac{3}{4}$ in. strip of back, of a controllable thickness, which keeps the cathode hung.



FIG. 8.—CURVED CHUTES FOR GRAVITY CHARGING.

Refinery, or Wire Bar Practice

From the stripping room, cathodes are delivered to cars or barges for shipment; or else to the wire-bar furnace charging floor, which is elevated above the furnace for chute charging, as later described. Up to a year ago, the individual cars of cathodes were pushed from stripping room to small elevators, lifted slowly, and pushed around by hand on the furnace charging floor. There has now been installed a small monorail

crane, which rapidly lifts the cathodes up through a small shaftway and then carries them farther, depositing them on the feed floor. The crane is also used during the immediate charging period, shifting piles of cathodes nearer the chutes, thus further reducing labor.

Figs. 8 and 9 give a good idea of the method of charging, which is a natural outgrowth of the Nichols series system. The cathodes produced are so long, narrow, thin, and light in weight as to suggest projecting them into the furnace in such a way as to land them flat on the furnace bottom. The advantages are obvious. Most important, the brickwork of the furnace is not exposed, for several hours daily, to intruding cold air through the wide-opened charging doors. Likewise, the sides and

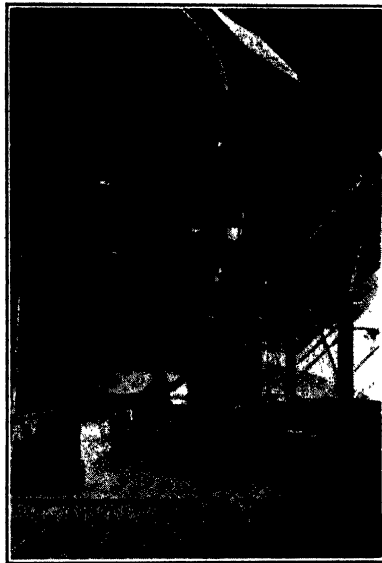


FIG. 9.—CHARGE FLOOR OF WIRE-BAR FURNACE WITH MONORAIL ABOVE.

door jambs cannot be damaged by a careless operator, as occasionally happens under the best conditions with a charging machine. The elimination of the initial expense and the maintenance of the charging machine, together with the space it requires, is a further advantage. A strong argument for chute charging is that it helps to keep the furnace on a regular 24-hr. cycle. Here again the facts speak for themselves. At Laurel Hill, the furnace produces from 700,000 to 750,000 lb. of copper each day, every day in the month if necessary (except for some major repair operation). If one of the many minor things happen to "throw the furnace back" an hour or two, the next day the furnace is right back on schedule. At any rate it can be relied on to gain back gradually the time lost, whereas great difficulty is usually experienced in holding the

ordinary type of furnace to a 24-hr. cycle, to say nothing of 23-, 22-, or 21-hr. This is due to the heat retention, as well as to the rapidity, of chute charging. As to the latter, daily routine of charging at Laurel Hill is about as follows: 300,000 lb. are introduced from 3:00 to 3:30 p. m., 220,000 lb. from 6:00 to 7:00 p. m., 130,000 lb. from 9:10 to 9:50 p. m., and the balance of 70,000 lb. from 11:00 to 11:30 p. m. Twenty-seven man-hours of labor are employed for the work, including the time of the men who seal up with clay and old brickbats the narrow apertures where the chutes open into the furnace.



FIG. 10.—WIRE-BAR CASTING LADLE AND STRAIGHT-LINE CASTING MACHINE.

The wire-bar casting ladle and straight-line casting machine are shown in Fig. 10.

Further Improvements

Plans are definitely under way for further improvements in refining methods at Laurel Hill. In the anode department, authorization has been given for the immediate erection of a unit, to consist of a large semi-continuous receiving, melting, and slagging furnace, and two smaller furnaces, reserved for refining, poling and casting only. Material benefits are expected, the new unit taking the place of four present furnaces. It will be connected to a single, large, efficient waste-heat boiler. Important heat economies will be effected, steam production being practically continuous instead of intermittent. As in the case of most copper refineries, waste-heat steam from anode furnaces is now produced in large quantities during the night hours; whereas during the daytime, when steam is most needed, most of the furnaces are casting or charging and very little waste heat is produced. A coördinated unit, as described,

will give a more nearly ideal steam producer from a powerhouse standpoint.

Consideration is also being given to the use of a mechanically operated ladle for casting the thin anode instead of doing the work by hand, with resultant possibility of increasing size of the anode-refining furnace and, later, increasing the size of the anode itself.

In the assembly department studies are being made as to the advisability of installing a mechanical straightener and punch machine.

Another improvement, which is expected to be in operation during the summer of 1925, is a "Ferris-wheel" casting machine. The large furnaces are equipped with straight-line casting machines and one of them is to have a second tap hole on its opposite side. This will connect with the ladle for a casting machine rotating in a vertical plane, which will cast, during the regular major casting time of the furnace, about 50 to 75 tons of special shapes. This revolutionary step in copper casting has been taken not only because economy of floor space made the new wheel very attractive for the particular problem to be solved, but also because it is believed that this machine will make a better casting, as experiments carried on several years ago conclusively proved was possible for this type of machine. The ladle is located in such a way that the semimolten copper in the mold, after being poured from the ladle, will travel several inches almost vertically (only a very few degrees off the perpendicular). This should effectively eliminate any "wave," "roll," or "edge" on the copper, in case of any jerky stop or start of the wheel.

CONCLUSIONS

1. It has been found possible to treat blister much more impure than that formerly used in the Nichols Copper Co.'s series system of copper refining at Laurel Hill.

2. This has been brought about by changing spacings between electrodes when analysis of the blister requires it, but especially by carefully regulated electrolyte treatment with suitable addition agents, keeping cathode deposit smooth.

3. Under these conditions, it has also been found possible to permit a material increase in the percentages of arsenic and antimony in the electrolyte.

4. Power consumption is remarkably low, a five-year average being 341 lb. of copper deposited per kilowatt-day, as compared with 200 lb., which would be considered very good work in multiple practice.

5. Reenforced-concrete tanks, lined with asphalt mastic, are used for the electrolytic work, and the lining is not attacked at working electrolyte temperatures, which are carried as high as 125° F.

6. Silver and gold losses for the above five-year period, with anodes running 30 oz. silver and $\frac{1}{2}$ oz. gold, were 2.4 and 2.0 per cent., respectively.

7. Instead of the 100 per cent. hand labor formerly used, many operations, especially tank loading and unloading, have been mechanized and important further steps along these lines are shortly to be taken, particularly in the furnace departments, where a melting furnace and a casting wheel of "Ferris wheel" type will shortly be in operation.

8. Low original cost of a Nichols series tank room is emphasized, only 200 sq. ft. of floor area being required per ton deposited per day, equivalent to about three-fifths of multiple requirements. There is also a much smaller copper tie-up in busbars, hanger bars, and other auxiliary apparatus. All these items materially reduce initial capital construction outlay, and interest, depreciation, and amortization charges during the period of operations.

9. The result of the practices described, and of the improvements, completed and projected, will be to combine with the sound basic technical advantages of the Nichols series system, design and equipment peculiarly fitted to make the most of these advantages, and to continue the place of this series process in the forefront of copper-refining metallurgy.

ACKNOWLEDGMENT

The author acknowledges his indebtedness to the Executive Committee and Officers of the Nichols Copper Co., through whose courtesy permission was obtained to publish this paper, and to the assisting members of the staff for their help in its preparation, especially to Mr. F. E. Lee, Works Manager, Mr. W. H. Hubbard, Jr., Assistant General Superintendent, Mr. Eugene Fitzpatrick, Chief Chemist, and particularly to Mr. J. S. McClenahan who has been in charge of the electrolytic refinery while most of the developments have taken place, who has been directly responsible for many of the improvements described, and who furnished much of the data on addition agents, as well as the photographs.

DISCUSSION

M. H. MERRISS.—With regard to silver and gold losses, it is noted that they are considerably higher than the multiple on a percentage basis. We have a large and essentially a very deep tank, which has five long, thin anodes in it, as you have noted from the paper. The silver mud that is electrolyzed has to drop through $4\frac{1}{2}$ ft. of very narrow spacing between two electrodes, so it has a very good chance of being caught. That, of course, is the reason for the comparatively high percentage losses in silver.

I can say that a very large percentage of that 2 per cent. silver loss, is lost near the bottom of the cathode. (For normal multiple copper

refining work 1 per cent. may be considered the normal silver loss.) So it is also self-evident that if one were called upon to design a plant for a particularly high silver blister, from a broad economic standpoint it might be well to have a comparatively shallow tank with an anode that was very much shorter, so that the opportunity for the silver mud to settle on the cathode would be minimized. If you did that you would tend to counteract your other advantages such, for instance, as low installation cost per ton of copper refined. There is a tank room in operation now of this design, although it was not so designed on account of high silver content. It is at Boleo in Lower California. The tank is very shallow and the anode also, and the silver losses must be very low.

A. L. WALKER, New York, N. Y.—In the old Guggenheim plant, afterward the American Smelting & Refining Co., at Maurer, near Perth Amboy, the anodes were 3 ft. deep and 2 ft. wide. High argentiferous copper bullion was treated at that plant. We found the loss in silver, even in the multiple system, was quite high. After conducting a series of tests we determined that fully one-half of the silver in the cathode was in the bottom 9 inches. In building a new plant in 1902, we turned the anodes around 90°, making them 3 ft. wide and 2 ft. deep, instead of 2 ft. wide and 3 ft. deep. We did this to save the excess amount of silver which would be caught on the surface of the deeper cathodes due to falling anode slime. It was a question of saving silver as against floor space required.

In the early days it was always considered that only very pure copper bullion could be treated by the series process. I think the results of the work that has been done by the Nichols Copper Co. in recent years shows that the limit for impurities can be materially increased. It has been found possible to use an electrolyte containing very much higher impurities even in the series system. I do know, however, that it is more difficult to treat a high silver copper in the series process than with the multiple. The silver losses are bound to be greater.

E. L. JORGENSEN, Irvington, N. J.—I have found that the large amount of values usually found near the bottom edge of the cathode in the multiple system can be overcome by making the cathodes considerably longer. I would like to ask Mr. Merriss if the very bottom edge of the cathode contained a higher percentage of silver, i. e., if you took a section 6, 8 or 10 in. from the bottom and analyzed it?

M. H. MERRISS.—With us, the cathode is not enlarged on the edges the way it is in the multiple if you work with too large an anode. It is almost flat, and we have never cut off the bottom half-inch and analyzed it for silver. I agree with Prof. Walker that the percentage of silver loss is bound to be higher in the series than in the multiple, due to the closer spacing. All I wanted to bring out was that the ratio was not necessarily just 1 to 2.

A. L. WALKER.—It is a regular practice in the multiple system to make the cathode deeper than the anode so that the cathode projects from $\frac{1}{2}$ to 1 in. below the lower edge of the anode.

A. F. SCHNEIDER, New York, N. Y.—It makes a great difference if the anode has only 30 oz. or if it has 150 oz. Percentage is not a criterion. When Prof. Walker spoke of the high silver content of the anodes I wondered if his percentage would be the same. I think, not at all. It is a question of dollars and cents.

M. H. MERRISS.—That point is covered in the paper; the actual silver and gold contents are given, and the following also appears:

Furthermore, individual results obtained from time to time have proved conclusively that the percentage loss of precious metals would decrease materially with an increase in precious metal content of the anodes.

When the anode is higher, the percentage loss is less. The dollars per ton loss is greater.

A. L. WALKER.—In 1902, when the plant I referred to was built, the copper bullion assayed 350 oz. I know at times we received bullion from Mexico which ran as high as 1000 oz. per ton. The silver loss was a very important proposition. My recollection is that the loss was under 1 per cent. Mr. Witherell says definitely his recollection is that it was 0.6 per cent.

S. SKOWRONSKI, Perth Amboy, N. J.—One point that the author did not bring out as forcibly as possibly in the paper, is that while the author has undoubtedly refined a lower grade of bullion than hitherto thought possible by the series system, he has done so at the expense of increased spacing, which will increase the voltage on the tanks, and then reduce the output of copper per kilowatt day.

The great advantage of the series system over the multiple system is that a closer spacing is possible with a corresponding decrease in voltage. If the spacing is increased, the natural advantage of the series system over the multiple system is thereby decreased.

There is in the Metropolitan district a refinery operating with 98–98.5 per cent. anode, and yet obtaining 220 lb. copper per kilowatt day, using the multiple system. A direct comparison of the series system versus the multiple system with this low-grade anode would be interesting.

F. R. PYNE, Perth Amboy, N. J.—Regarding Mr. Skowronski's statements: One point which has not been brought out relative to power saving with the series system is the absence of contact losses. You have practically no contact losses in the series system, whereas you have from a 25 to a 30 per cent. loss in the multiple system. Possibly it may amount to 5 per cent. in the series system. The series system operating on practically equal spacing as the multiple system has the advantage in requiring much less floor space per ton of copper produced per day. The

normal multiple tank holds from 15 to 18 tons of copper, the old wooden series tanks about 27 tons, and the large concrete ones 50 tons.

With the series system you have the elimination of the old bugbear of starting sheets, 2 or 3 months' supply of which must be carried.

There are some serious disadvantages to the series system; that is, on the preparation and the casting of the anode and the stripping of the back. There are many points, relative to labor, which could be satisfactorily solved provided some one would be willing to put up the requisite time and money. The series system, unfortunately for the copper refining world in general, has been surrounded by a great deal of secrecy for reasons best known to those who operate the plants. There was no interchange of ideas. If there had been, and had the attention been given to the series system that has been given the multiple, I very much doubt whether the multiple system would be as predominant as it now is.

Anaconda Electrolytic White Lead

BY R. G. BOWMAN, EAST CHICAGO, IND.

(Salt Lake City Meeting, September, 1925)

DISCUSSIONS of processes for the manufacture of white lead generally open with the statement that white lead is the oldest chemical pigment known to man. This fact is of more than historical interest; in the light of the present extensive use of white lead, it indicates that the compound possesses characteristics that make it unique among white pigments, and superior to all in its particular field. A greater variety of processes have been proposed for manufacturing white lead than for any other one chemical compound. Only a few of these processes have come into commercial use, however, and a large part of the present production here and abroad is made by the process used in ancient times.

The outstanding disadvantages of the old process are that it is slow and laborious, affords no control of the product, and yields at best an impure material lacking in uniformity. Improved processes, sometimes classed all together as "quick processes," have had as their main object the shortening of the time required. Most of them accomplish this and some have yielded a superior product as well, but only two or three are now in use commercially.

For centuries the manufacture and mixing of paints have been treated as an art, and the practice has been much influenced by tradition and precedent. There is a reluctance to abandon old materials for this purpose, and as few new uses for white lead have been developed, the adoption of the quick processes has been slow. The electrolytic production of white lead is not new, a large number of processes and forms of apparatus have been proposed and patented within the past 25 years, all directed toward the production of white lead, wholly or in part, by electrolysis. One or two of these processes were tried commercially but proved unsuccessful.

PROCESS

The Sperry process, used by the Anaconda Lead Products Co., is the invention of Elmer A. Sperry, and was worked out to a commercial basis at the East Chicago plant. It resembles, in a general way, earlier methods, but embodies the features that make it possible to operate

continuously and to produce a uniform product, the character and composition of which are under complete control. It has made possible the rapid production of white lead of a degree of chemical purity and brilliant "whiteness" superior to any produced by other methods. These properties of the product are independent of the purity of the metallic lead used.

The Sperry process is not a process for the production of white lead alone, but a basic method of producing an insoluble salt of any metal by a continuous electrolytic process. Application of the method to lead salts, and to white lead in particular, was selected on account of the staple character of the product, calling for production on a tonnage basis. The process is a combination of electrolysis and chemical precipitation, in which the precipitation is a secondary reaction and the composition of the reagents and of the precipitate are controlled electrolytically. It is unique among electrolytic processes, in that it yields a solid product that is neither an anode nor a cathode deposit and is removed continuously.

As applied to white lead, the process is carried on in a cell having a lead anode and an iron cathode, separated by a porous diaphragm. The anode is surrounded by an electrolyte—the "anolyte"—containing sodium acetate and a very small amount of sodium carbonate. The cathode is surrounded by a similar electrolyte—the "catholyte"—containing sodium acetate and a relatively large amount of sodium carbonate. Each electrolyte is maintained in rapid circulation about its electrode. The circulation systems of the two electrolytes are entirely independent and no communication exists between catholyte and anolyte save through the diaphragm in the cell.

The action occurring when the current is applied may be described, simply, as follows: The lead is dissolved from the surface of the anode, electrolytically, as lead acetate and is immediately reprecipitated as insoluble basic carbonate, $2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$, by the sodium carbonate in the anolyte, thus restoring the sodium acetate but depleting the anolyte in CO_3 ion. The proper concentration of CO_3 is restored and maintained constant by passage of this ion through the diaphragm from the catholyte, which in turn becomes impoverished in CO_3 . The anolyte enters the cell clear and leaves carrying the white lead in suspension, but with no change in composition. The catholyte enters the cell high in Na_2CO_3 and low in NaOH , and leaves low in Na_2CO_3 and high in NaOH . The CO_3 is restored by carbonating the catholyte at one point in its circulation outside the cell.

The white lead produced in suspension in the anolyte is removed from the cell continuously by the circulation of the anolyte. It is separated from the solution by settling and filtration and the clear anolyte is returned to the cell. The white lead thus removed is washed, dried, pulverized, and barrelled for market.

This, in brief, is the process, without entering into the details of the electrochemical phenomena occurring in the cell; in operation, the process is considerably more complicated. The balance to be maintained for continuous operation is rather delicate and there are a large number of factors slight variations of which will interfere with operations, either immediately or in a cumulative manner. This is merely the converse of one of the chief advantages of the process; namely, its flexibility and the close control of composition, purity and physical character of the product which it affords. In this respect it does not differ greatly from other electrolytic processes, where a continuous closed cycle of circulation is maintained; however, when approaching it as a new process in the development stage, the array of variable factors appeared rather formidable and a great deal of experimental work has been required to establish a simple method of control, and means for protecting the operation and the product against unavoidable variations in raw materials and operating conditions. This control has now been so far simplified and standardized that all important factors are centered in the analysis of two solution samples, and an arbitrary relation or ratio between certain constituents. These analyses are simple alkalimetric titrations and are made by an operator at the plant.

PLANT

Materials of Construction

The circulating electrolytes used are alkaline or neutral solutions, and at first the problem of handling appears to be much simpler than in the case of an acid and highly corrosive solution; however, the extreme purity required of the product limits the selection of materials that can be brought into contact with it or with the circulating solutions.

The solutions are destructive to wood, due to the saponification and removal of the resins. Most paints and waterproofing coatings either contain saponifiable oils or are slightly acid, and are gradually destroyed. Bakelite and other phenol condensation products are soon destroyed. Concrete is penetrated and gradually disintegrates due to crystallization of salts and to electrolysis of the metal reinforcement. Porcelain and stoneware are only slightly affected but have other limitations. The only satisfactory nonconducting material found for contact with these solutions is rubber, in various degrees of hardness. Hard-rubber pipe fittings, soft-rubber hose, and wood launders lined with soft-sheet rubber are used for handling solutions at all points where it is necessary to reduce the electrical conductivity of a solution line. Hard-rubber is used, also, in the construction of the supporting frame for the cathode diaphragm.

Pure copper, pure lead, and, in some cases, cast iron are unaffected by the solutions; brass and bronze are used in the present plant for much of

the piping; however, these are not entirely unaffected as a local electrolytic action is set up by the two metals forming the alloy.

Considerable experimental work has been done on protective coatings for wood and concrete. An enamel-like asphalt coating for concrete has been developed; this has been applied to all tanks and cells in the plant and has proved satisfactory in all cases where the concrete can be protected from entrance of moisture behind the coating. Asphalt coatings for concrete have failed completely in all tanks below ground level and wherever the concrete is exposed to moisture that enters and forces the coating off of the surface.

Equipment and Operation

The East Chicago plant is the first commercial-size unit for producing white lead by the Sperry Process; it was completed and placed in operation in January, 1920. The plant was designed for a capacity of 10 tons of dry white lead per 24 hr. While the capacity of the electrolytic cell can be calculated rather closely, and had been established by experiment in a small one-cell laboratory plant, the capacities of standard settling, filtering, and drying equipment, as applied to the product, were unknown. As a result, some of the equipment installed was found to have a much greater capacity than estimated, when operated continuously. It was also found possible to operate the entire cell room continuously at a higher current density than estimated, resulting in more than doubling the capacity of this department.

After the initial difficulties had been overcome and continuous operation established, the capacity of the drying department was brought to an equality with the remainder of the plant, and other adjustments in equipment made to provide storage space between departments. The plant is now producing 26 tons of dry white lead per day. This production is determined by the working capacity of the present motor-generator supplying current to the cells, but does not represent the capacity of the present cell design, which is about 1500 lb. per cell day.

The plant was designed essentially as an operating unit, but has been used to some extent for a continuation of experimental work. The cell-room equipment is peculiar to the process and presented certain operating problems of its own. Equipment in other departments was selected with a view to provide standard machinery that fulfilled the requirements and insured protection of the cell-room product. Selection of more efficient equipment in these departments was left for a later development. This standard machinery is still in use, but considerable experimental work has been done on other equipment designed to reduce labor and operating costs and to introduce mechanical handling of the product throughout. The installation of this machinery forms part of the pro-

gram of extension of the present plant. A general exterior view of the plant is shown in Fig. 1.

Buildings

The main building, housing the cell room, settling, and filtering departments, is of brick and steel 78 by 87 by 27 ft. high. The dryer tunnels are of brick and extend from the main building to the pulverizing and barrelling department, which is a frame building. Additions to the main building, to house additional solution tanks, pumps and storage bins, are of frame and corrugated iron. The substation is of brick and steel and the boiler house and miscellaneous out-buildings are of corrugated iron.

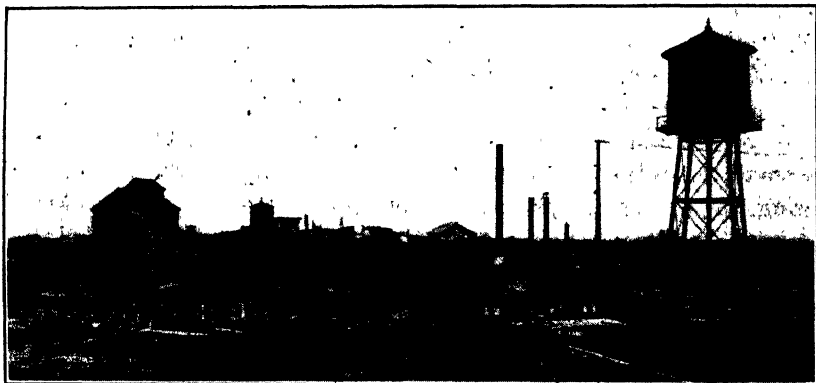


FIG. 1.—EXTERIOR VIEW OF PLANT.

The solutions handled are rather destructive to building materials. Excessive condensation of vapor, combined with alkali dust, attacks the metalwork and makes frequent repainting necessary. Good ventilation, blast heating, and a heavy felt roofing on the main building have reduced this trouble considerably.

Anode Molding

The anode is a rectangular lead plate 21 by $30\frac{1}{2}$ by 1 in. and weighs 250 lb. Projecting lugs are cast at the two upper corners for supporting the anode in the cell. It resembles the standard anode of copper refining, but the lower physical strength of lead requires a heavier lug section, to resist bending. Anodes and common pig lead are molded, as required, from the same furnace, at the Parkes Process refinery of the International Lead Refining Co. and are transferred, on rack cars, to the white lead plant, 1000 ft. distant.

The anode is molded in a cast-iron mold 1 in. deep, set horizontally; twenty molds are arranged in an arc below the tap of a reverberatory furnace. Lead flows from the furnace through a 2½-in. plug-cock connection to a pivoted-head pot and is delivered to the molds through a 2½-in. pipe launder swinging radially from the head pot. The stream is stopped after molding each anode by lifting the delivery end of the launder. The anode is chilled with water, sprayed on its surface, and is ejected from the mold by a small plunger operated through a trigger valve by compressed air, which raises the lugs free from the mold. The anode is picked up by a small air hoist, mounted on a radial traveller, and transferred to a rack. From the racks, groups of twenty-five anodes are



FIG. 2.—GENERAL VIEW OF ANODE MOLDING.

transferred to the straightening press by the overhead cranes serving the refinery. A general view of the anode molding operation is shown in Fig. 2. The capacity of this equipment is approximately 20 tons of anodes per hour.

Anode Pressing

The soft lead anodes are easily bent and deformed when being removed from the mold and in handling. Before delivery to the cell room, they are straightened in a press located at one end of the refinery. This is a horizontal press having a single cylinder 10½ by 23 in. and is operated by compressed air at 90 lb. pressure. Two anodes are pressed at one time. A small compressed-air jib crane serves the press.

After pressing, the anodes are arranged on rack cars in their proper spacing for placing in the cells, each car holds two sets, of eighteen anodes each. The cars are delivered to the cell room over a short industrial

railway using a gasoline locomotive. Scrap returned from the cell room to the refinery for recasting is handled with the same equipment.

CELL ROOM

The cell room is 40 by 74 by 16 ft. high, from operating floor level to the hoist monorails. Below the operating floor is a shallow basement 5 ft. deep, the floor of which is at ground level. The building is of brick and steel, with felt-insulated wood roof to prevent condensation. It is lighted on three sides by steel sash; the fourth side is open to the tank room. The cell-room interior is shown in Fig. 3.

The forty-eight cells are arranged in six rows of eight cells each, with operating aisles between. Each cell is supported independently upon concrete piers, rising from the basement-floor level. The top of the

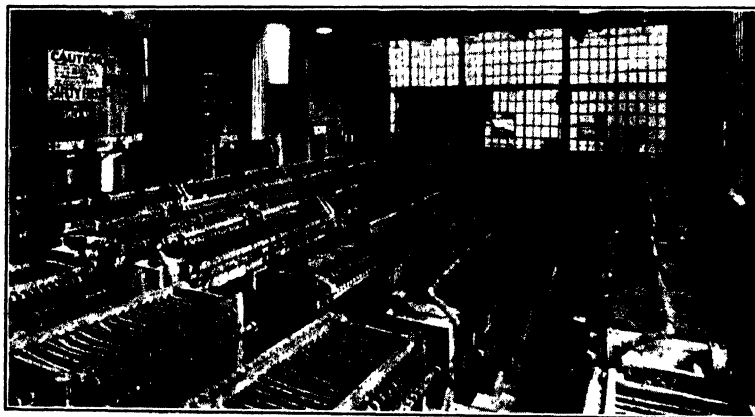


FIG. 3.—INTERIOR OF CELL ROOM.

cell is 29 in. above the operating-floor level. The operating floor is merely a wooden deck laid in movable sections and supported from the cell piers.

Each row of eight cells has, at one end, an anode wash tank and an anode storage rack. The industrial track handling anodes and scrap from the refinery enters and passes across one end of the cell room, delivering anodes to any of the storage racks. Each row of cells is served by a 3-ton Sprague electric monorail hoist, travelling over the anode track, storage racks, wash tanks, and cells. A transfer bridge at one end of the cell room permits the interchange of hoists between rows.

Cell

The construction of the cell is illustrated in Figs. 5, 6 and 7. The cell proper consists of a rectangular tank with hopper bottom, built entirely

of reinforced concrete, ("gunnite"). The inside dimensions are $24\frac{1}{4}$ by 54 by $33\frac{5}{8}$ in., with a shallow hopper bottom leading to a 3-in. horizontal discharge. The walls are 3 in. thick and are reinforced with wire mesh.

The discharge is connected through an inverted siphon to a rectangular overflow box of concrete, placed at one end of the cell. The box has an inlet and an outlet compartment separated by a movable wood dam, the height of which controls the level of solution in the cell. The interior of the cell and overflow box is lined with asphalt enamel, to prevent

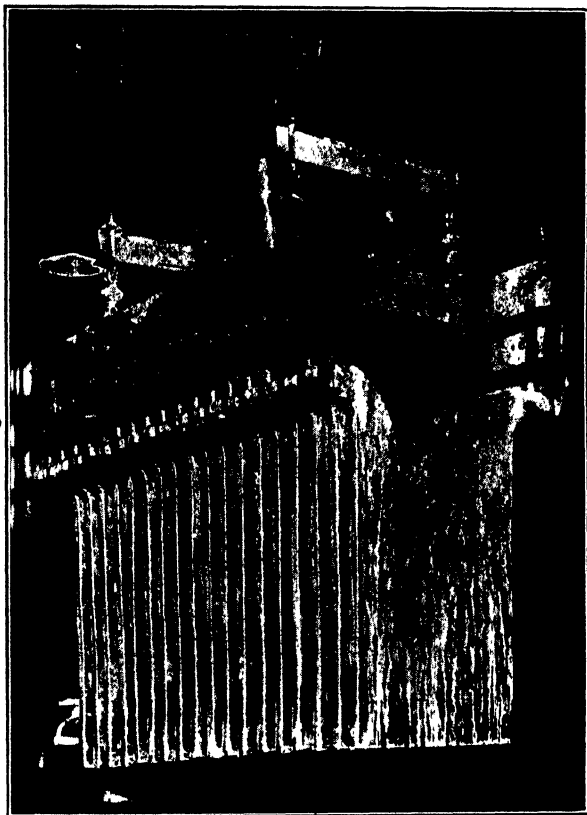


FIG. 4.—SET OF EIGHTEEN ANODES.

penetration of the concrete by the solution, and consequent electrolytic corrosion of the reinforcement.

The anode and cathode busbars are supported on the cell body as shown. Each bar is of copper $1\frac{1}{4}$ by 4 in. in cross-section, and runs the full length of the cell. The anode busbar rests on insulating blocks on the rim of the cell at one side, it has no rigid attachment to the cell body, but is an extension of the cathode busbar of the adjoining cell, which is bolted to the cell.

The anode hangs in the cell, supported by its lugs, one of which rests on a block of hard rubber on the rim of the cell and the other on the anode busbar. The busbar carries on its upper face a single sharp rib, which cuts into the soft metal of the anode lug and makes a connection of low electrical resistance. Each cell holds eighteen anodes, spaced 3 in. center to center.

The cathode, with the diaphragm and supporting frame, form a separate unit, which is described later. The cathodes are supported in the cell at 3-in. centers. The lower corners of the frames rest on horizontal ledges formed in the body of the cell, and the spacing of the frames

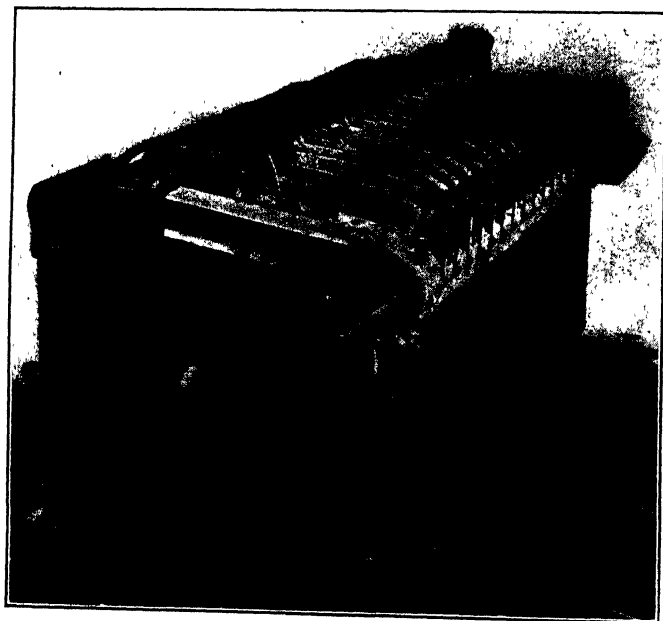


FIG. 5.—ELECTROLYTIC CELL.

is maintained by notched wooden strips attached to the inner walls of the cell, as illustrated. A copper busbar, mounted on the upper edge of the cathode sheet, projects at one corner of the sheet and is bolted and soldered to an insulated copper strap, which passes under the anode busbar and is attached to the cathode busbar. The latter is supported on insulators bolted to the side of the cell, as shown.

When a cathode is removed, the soldered and bolted joint is easily broken and remade by the use of a tool that short-circuits the cathode to an anode in an adjoining cell, thus heating the joint sufficiently to melt the solder. Each cell contains seventeen cathodes, leaving the outer face of each end anode inactive.

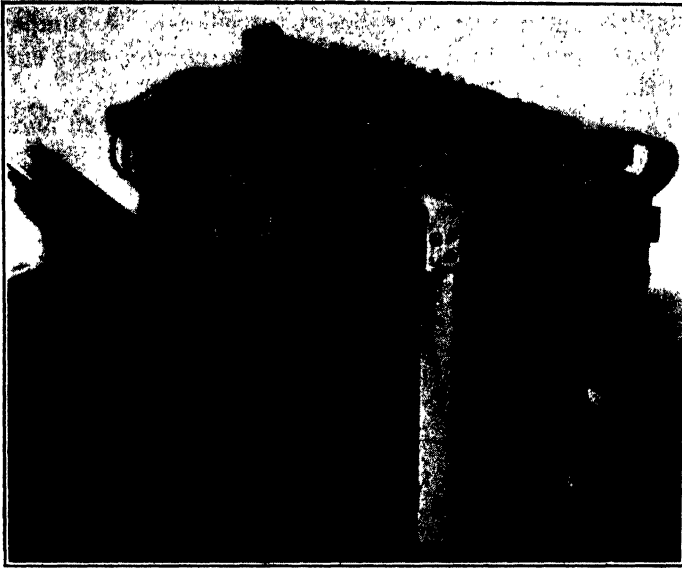
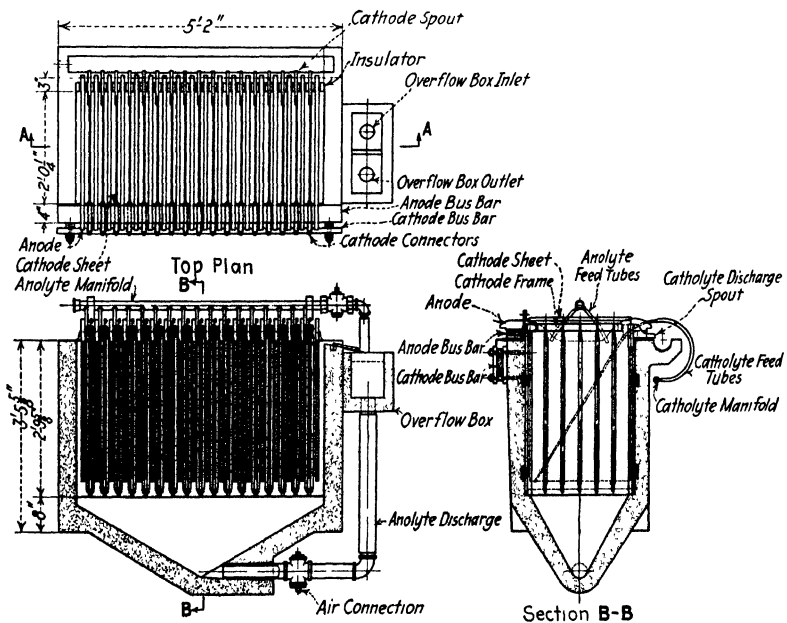


FIG. 6.—ELECTROLYTIC CELL, SHOWING CATHOLYTE DISCHARGE AND OVERFLOW BOX.



Section A-A
FIG. 7.—ASSEMBLY VIEW OF ELECTROLYTIC CELL.

The entire forty-eight cells are connected in series. Current enters the cell room by a line of copper busbar $1\frac{1}{2}$ by 4 in. in cross-section and 25 ft. long, from generator switchboard to cell A-1. A jumper-bar on each cell short-circuits the anode and cathode busbars, thus cutting the cell out of the circuit when desired for any purpose.

The cell illustrated and described is the original design and the one now in use. Certain defects and weaknesses have been recognized in the

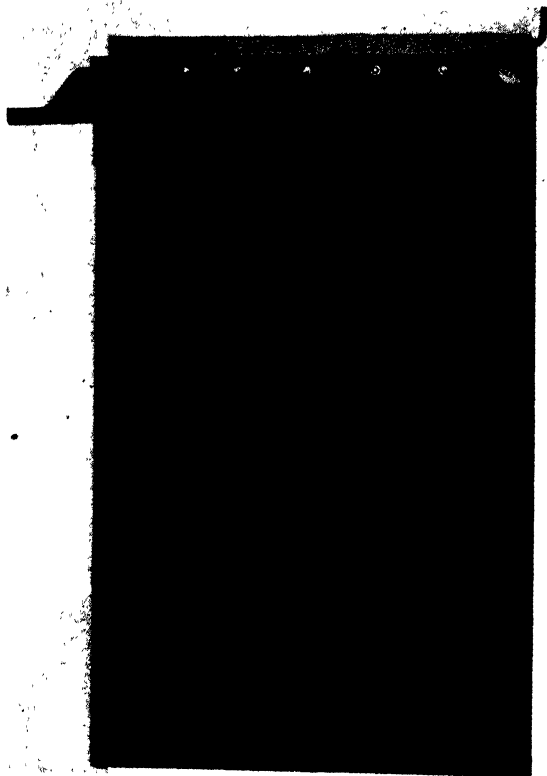


FIG. 8.—CATHODE FRAME AND DIAPHRAGM.

design, and their remedies have been worked out. These changes will be embodied in any new cells constructed, however, the general design has been found highly satisfactory and well adapted to the process.

CATHODE FRAME AND DIAPHRAGM

The Sperry process is essentially a diaphragm process. The formation of carbonates of lead, and of other metallic salts, in a manner similar to that in this process is possible in a one-solution cell, without the use of

any diaphragm, but the continuous production of basic carbonate of lead of uniform composition, in commercial quantities, is the thing that has been made possible by Sperry. This has been accomplished by the application of the diaphragm type of cell using two distinct solutions.

To anyone familiar with electrolytic processes, the subject of diaphragms is common, and, to those familiar with diaphragms, rather unpleasant. Many successful laboratory processes dependent on a diaphragm cell have failed commercially because of the lack of suitable diaphragm material, which performed the functions of a diaphragm and was at once durable and cheap.

In a diaphragm-type electrolytic cell, the anode and cathode are placed in separate compartments in the cell and are surrounded by solutions of different characters and compositions. The two compartments are separated by a diaphragm having a degree of porosity suited to the requirements of the operation being carried on. Economy of construction and operation require that the following conditions be fulfilled:

The anode and cathode must be parallel and as close together as possible.

The diaphragm must lie directly between the anode and cathode, must be as thin as possible, and must offer as little resistance as possible to the passage of the electric current. The diaphragm support must be tight and allow no leakage or intercommunication between the two compartments or solutions, except through the pores of the diaphragm. There must be between the anode and cathode no inert obstructions that will have the effect of reducing the effective area of the electrodes. There must be between the two electrodes no active conducting material that can act as an extension of either electrode and thus cause a local reduction of the spacing.

The diaphragm must not be in electrical contact with either the anode or cathode.

A free and uniform circulation of solution about both electrodes must be maintained, and provision must be made for the escape of gas generated at either electrode, without causing frothing or boiling over of the electrolyte.

There must be no obstruction that will allow the accumulation of solid matter from either solution between the electrodes.

It is evident that the comparatively thin flexible material used for diaphragm, is incapable of supporting itself in a perfectly flat form over a wide area, and that a slight difference of pressure on opposite sides will bring it into direct contact with one of the electrodes. A supporting frame for the diaphragm that fulfills the other necessary conditions, is therefore required.

A great variety of materials have been tried for diaphragms for the Sperry process, and a number have been found entirely suitable from a

chemical and physical standpoint, so far as the requirements of the process itself are concerned. The questions of strength, durability, and cost have narrowed the field to a small number. Having selected a material, the design of a satisfactory support has led to the development and discarding of a great many designs of cathode frames. The early dia-

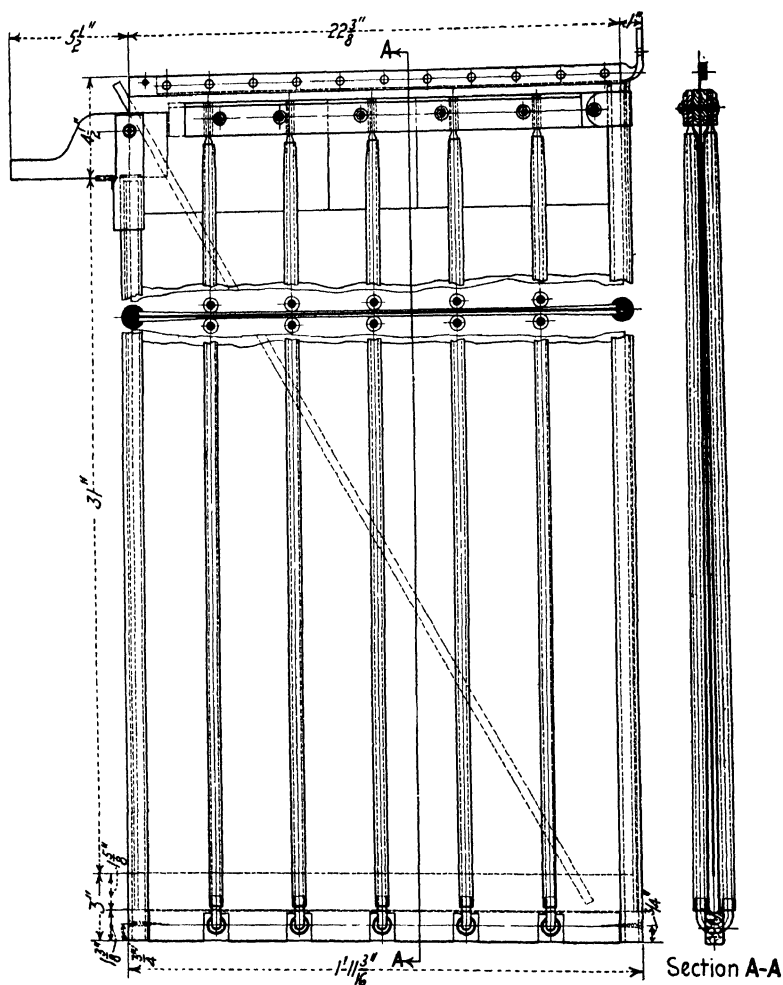


FIG. 9.—CONSTRUCTION OF CATHODE FRAME AND DIAPHRAGM.

phragms were made of parchment paper. This was replaced by cotton duck, parchmented by immersion in sulfuric acid. The present diaphragm is a heavy linen duck, tightly woven, and similar to the material used for water bags.

The present form of cathode frame is shown in Figs. 8 and 9. The essential feature is the forming of a water-tight diaphragm cell using the

diaphragm material alone, and eliminating all bolts and similar fastenings below the solution level. The frame structure then becomes merely a support, and the loosening of its joints or deterioration of its material will have no effect on the tightness of the diaphragm.

The diaphragm material is formed into a flat bag or envelope by stitching. The cathode sheet is fitted with edge strips of non-conducting material and is slipped into the envelope, which is made of the proper size to fit snugly over the cathode without undue tension, such as might increase its porosity. The depth of the envelope is slightly greater than the length of the cathode sheet, to allow space at the bottom for the distribution of the incoming catholyte, and also for accumulation of sediment.

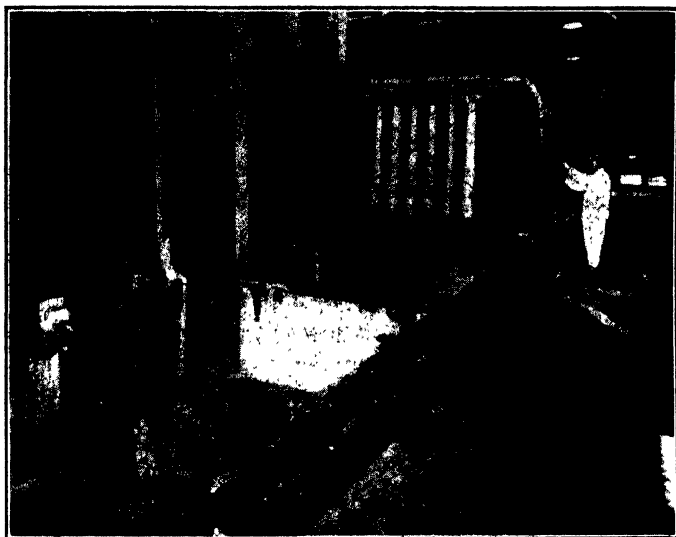


FIG. 10.—MOORE FILTER.

The two faces of the diaphragm are supported by a grid of vertical stayrods of non-conducting material attached to the frame at the top and bottom. The thickness and spacing of these stayrods is such that even when resting against the anode the normal bulge of the diaphragm between rods will not bring it into contact with the anode surface. The design of diaphragm supports has received much attention, and buttons, grids, and networks of various materials and designs have been tried and discarded. The present form of stayrod is merely a 0.34-in. brass rod inserted into a $\frac{3}{8}$ -in. hard-rubber pipe.

Cathode Frame Details

The diaphragm envelope is formed by stitching two sheets of linen together on three sides, leaving the top open. A stirrup of linen, open at

both ends, is stitched to the bottom edge to receive the bottom bar of the frame. The linen at the top of the frame extends above the solution levels and is subjected to alternate wetting and drying, and concentration of solution by evaporation, which soon rots the fabric; this portion is therefore protected by heavy rubberized cloth which is stitched to the linen.

The cathode sheet is of 16 gage steel plate and carries two edge strips, consisting of $\frac{1}{4}$ -in. hard-rubber pipe slit along one side and fitted over the edge of the sheet. The side bars of the frame consist of $\frac{3}{4}$ -in. hard-rubber pipe, slotted out on one side to leave about three quarters of the circumference intact. They are slipped over the edge strips of the cathode sheet with the diaphragm between the two. The side bar partly encloses the edge strip and is thus supported throughout its length.

The bottom bar is of paraffined maple, it is inserted in the stirrup on the bottom edge of the envelope, and its ends fit into the ends of the side bars, locking the corners of the frame.

The stayrods are U-shape and pass down one face of the diaphragm, through holes in the bottom bar, and up the opposite face. The upper ends are clamped under a metal strip bolted across the top of the frame. This strip closes the entire top of the envelope.

The catholyte overflow is a small steel spout welded to the upper corner of the cathode sheet. The sides of the spout are high and the opening into the frame is large, to allow the escape of hydrogen without overflow of froth. Catholyte is supplied to the frame through a $\frac{1}{4}$ -in. thin-walled hard-rubber tube, which enters at the upper corner and extends to the bottom corner, diagonally opposite to the overflow and below the lower edge of the cathode sheet.

The hard-rubber parts of this frame are cut from standard hard-rubber pipe, except a small corner piece. They are interchangeable and can be removed and replaced quickly when renewing the diaphragm.

Circulation of Solutions

The two electrolytes, anolyte and catholyte, enter and leave the cell and are circulated throughout the plant in two separate systems. No contact or mixing of the two solutions occurs except through the diaphragm between the anode and cathode.

In the operation of the plant it is convenient, at times, to add small amounts of catholyte to anolyte, or vice-versa, to control the concentration of solutions and to maintain a proper distribution of volumes. Proper connections for this interchange are provided, otherwise the piping systems are distinct.

Clear anolyte is supplied to the cell room by a single centrifugal pump, of 800 gal. per min. capacity, and is distributed to each cell through

a system of hard-rubber pipe and fittings and soft-rubber hose, supported below the operating floor. This piping system was originally of brass, but current leakage and electrolytic corrosion in all parts led to the substitution of rubber. Long lengths of hard-rubber pipe are avoided; fittings with nipples are used, and these are connected with lines of pure gum hose. This has proved to be a very satisfactory and flexible system.

Anolyte is supplied to the cell through a 1½-in. manifold distributor of hard rubber, supported on blocks that rest upon the tops of the cathodes, as illustrated. The solution enters at one end and discharges through eighteen short nipples on each side of the distributor. Short rubber tubes attached to the nipples hang down between the cathode sheets to deliver the solution without splashing. The rate of flow to the cell is from 16 to 18 gal. per min.

The feed manifold must be removed before the anodes or cathodes can be taken from the cell. Being of rubber, it is light and easily handled and the flexible hose connection allows it to be moved about freely.

The anolyte, carrying the white lead in suspension, leaves through the base of the cell, rises through the inverted siphon, and overflows the dam in the overflow box. The level of the anolyte in the cell is maintained as high as possible, to secure maximum immersion of anodes. The overflow lip discharges into the box with the normal discharge, but is used only as a safeguard, as maximum volume of discharge through the bottom is necessary to prevent settling and accumulation of white lead in the cell.

A ¼-in. low-pressure air connection enters the discharge line at its lowest point, this is used as an air-lift in cleaning the cell.

From the discharge side of the overflow box on the cell, the anolyte and white lead flow through a rubber hose to a system of rubber-lined launders, below the operating floor, and leading to a sump. In entering the sump, the combined discharge from all cells flows through a 100-mesh copper screen, to remove any foreign material that might fall into the cell and later cause trouble in the pumps. From the sump the anolyte, carrying approximately 0.5 per cent. white lead in suspension, is pumped to the thickener. This is a standard Dorr thickener 25 ft. in diameter and 10 ft. deep, with lead-covered steel mechanism and bronze rakes, the tank is of concrete lined with asphaltum enamel.

The white lead settles rapidly and is normally thickened to 20 per cent. solids. The thickened pulp is drawn from the thickener by a standard Dorco pump and delivered to a 7500-gal. concrete tank for storage prior to filtration. A small amount of settling and further thickening occurs in this tank upon long standing; the final pulp contains approximately 30 per cent. solids. The clear anolyte overflow from the Dorr thickener flows to the anolyte feed sump and is pumped back to the cell room. In warm weather the anolyte requires cooling, this is

done in a copper-tube heat interchanger, using city water as a cooling medium.

The normal volume of anolyte carried in the plant is 70,000 gal. The anolyte enters and leaves the cell at the same chemical composition, and there is no decomposition or fouling of the solution in the process. Changes in volume, due to leakage, evaporation, and the decomposition of water, are made up by addition of fresh water through the washing cycle at the filter and returned to the anolyte with the filtrate.

Catholyte is delivered to the cell room by gravity pressure from a 10,000-gal. tank, having a constant-head overflow, which maintains a pressure of approximately 12 in. of water at the point of delivery to the cell. It is distributed to the cells through a system of rubber hose and piping similar to that carrying the anolyte. At each cell is a $\frac{3}{4}$ -in. rubber manifold, supported on insulating blocks on the side of the cell, as illustrated. This manifold has seventeen $\frac{1}{4}$ -in. outlet nipples, and each nipple is connected by a soft-rubber hose 18 in. long to the feed tube of a cathode frame.

The catholyte is discharged from the frame through a spout and flows through a shallow launder in the cell body to a discharge pipe at one corner of the cell. A short length of hose delivers the stream to a rubber-lined launder running the length of the cell room, beside each row of cells. The launders deliver to a common discharge line of iron pipe leading to a sump. The rate of circulation of catholyte is approximately 3.5 gal. per min. per cell.

The catholyte discharge system was first made of iron and later of rubber piping and hose. The present combination of open spout discharge on the frame and open launders leading from the cells was adopted to eliminate difficulties caused by entrained hydrogen, which produced gas pockets in the lines and consequent overflows.

The spent catholyte discharged from the cell room is pumped from the sump to the carbonating towers, where it is restored to its original composition and is returned to the catholyte feed tank by a 250 gal. centrifugal pump.

Carbonating System

The catholyte is carbonated by passing down in a shower through towers against a rising stream of carbon dioxide. There are three towers of standard type; each consists of a concrete shaft 8 by 8 by $21\frac{1}{2}$ ft. high, inside, lined with steel. The base forms a sump, a 10-ft. section of the upper shaft is packed with a standard tower filling of vitrified tile. The catholyte is introduced at the top in a series of gutters with notched edges, and showers downward through the filling. Solution to the depth of 24 in. is kept in the base of the tower at all times. The bases of the three towers are connected through a common discharge line lead-

ing to a steel overflow box. This box is divided by a dam, with an adjustable weir and screen, over which the carbonated solution flows and returns to the system.

Carbon dioxide is produced by burning coke in a deep bed in the firebox of a 35-hp. locomotive-type boiler, which operates as a suction gas producer. The gas is drawn from the stack of the coke boiler through a wet cyclone collector, which acts as a cooler and removes dust, soot, and traces of SO_2 . It then rises through tile-filled towers, duplicates of the carbonating towers, where any remaining moisture or dust is collected, and then enters the fan. The fan is a 500 cu. ft. centrifugal compressor with a maximum pressure of 2 lb., it delivers gas to the three towers simultaneously.

The gas enters the tower under a perforated steel plate⁵ covering the bottom of the tower base, rises through the solution, and through the tile-filled portion of the tower, to be discharged to the atmosphere. The gas secured is clean, but a certain amount of CO_2 is dissolved out by repeated washing; the gas averages 12 per cent. CO_2 by volume. A carbon dioxide recorder is used for control.

FILTER

The white lead from the thickener is filtered and washed on a Moore filter, using four counter-current washes and one final wash with hot water. The primary requirements of the filtering operation are that the white lead be washed entirely free of all soluble salts remaining from the anolyte, and that this washing be under control at all times. It is also desirable, from the standpoint of economy, to secure as complete a recovery of these salts as possible and to deliver a cake of low moisture content to facilitate rapid drying.

The Moore filter was adopted for the original plant as it fulfilled the first requirements. Considerable experimental work has since been done on other types of filters, both intermittent and continuous, but none offers any substantial advantage over the Moore type, though the present equipment could be greatly improved and simplified mechanically. A general view of the Moore filter is shown in Fig. 10.

The present installation consists of a series of seven rectangular concrete tanks 7 by 7 by $7\frac{1}{3}$ ft. deep, over which the filter frames, or "baskets," are handled by a 4-ton, electric, monorail hoist. The basket has six leaves, each 5 by 6 ft. quilted in the usual manner and using fluted wood inserts. The supporting structure of the basket is made entirely of wood and brass, to prevent contamination of the product. Vacuum pumps, receivers, piping and hose connections follow the standard arrangement for filters of this type. Provision is made for operating four baskets simultaneously, though normal operation requires but two

Each tank is equipped with a grid of perforated pipes in the bottom, for agitation, a small blower supplies air at 5 lb. pressure to all tanks. Wash water is heated to 125° F. by steam mixing valves, as it is delivered to the tanks. A normal vacuum of 20 to 26 in. is carried on the line, representing about 14-in. vacuum at the filter basket.

The normal pulp drawn from storage, following the thickener, contains 70 per cent. anolyte solution and 30 per cent. white lead. A cake 2 in. thick, weighing approximately 4000 lb. (dry basis) is built from this pulp in 20 min.

The four counter-current washes, of 600 gal. each, build up to proper strength for return to the anolyte system in the washing cycle; the final wash of approximately 5000 gal. of pure water at 125° F. goes to waste.

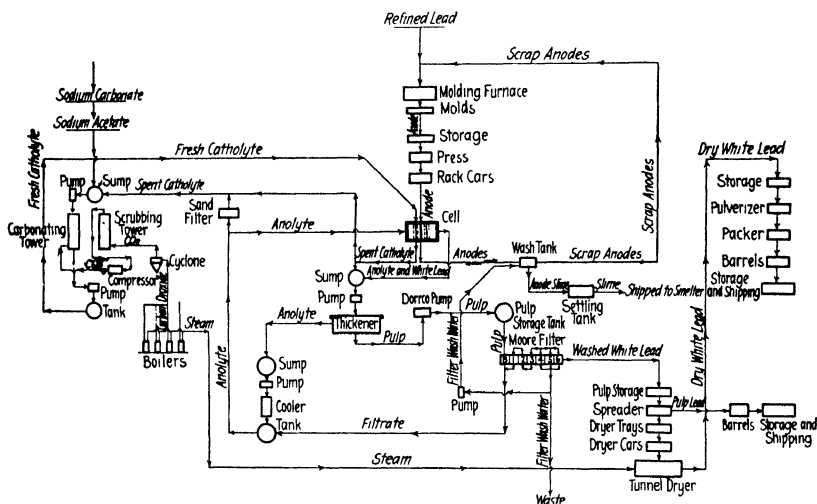


FIG. 11.—FLOW SHEET OF PLANT.

The length of the final wash on each cake is determined by sampling and titrating, at regular intervals, the wash water discharged from the vacuum receiver. Washing is continued until the soluble salt content of the discharge falls below a certain fixed minimum, the cake is then discharged into a small bin, from which it is elevated to a larger bin for storage preparatory to drying.

The normal washed cake discharged from the filter contains approximately 45 per cent. water. Because of the fineness and uniformity of the white lead, the cake at this moisture content is quite firm, and can be handled by a screw machine and inclined belt-and-bucket elevator.

DRYER

The washed pulp from the filter is stored in a rectangular wooden bin with two hopper-bottom discharge openings. Under each discharge opening is a ribbon machine, or spreader. The spreader resembles a

brick machine and consists of two parallel horizontal feed screws, which receive the pulp from above and force it out horizontally through a nozzle in the form of a flat ribbon, 2 in. thick and 22 in. wide. A sprocket and chain conveyor passes under the spreader nozzle. The dryer trays are placed end to end on this conveyor and carried under the nozzle; each receives a layer of pulp covering its entire surface. As the trays emerge from under the nozzle, they are lifted by hand and placed in tiers on the dryer cars. The dryer tray consists of a flat sheet of aluminum $\frac{1}{8}$ -in. thick, 22 by 36-in., perforated with $\frac{3}{16}$ -in. holes and surrounded by a rim $\frac{3}{4}$ -in. high of rolled aluminum shapes, riveted to the sheet.

The dryer cars are of steel, of standard pattern, $3\frac{1}{3}$ by 5 by $5\frac{3}{4}$ ft. high. Each car has rack space for twenty trays in two tiers of ten trays each, spaced 5 in. apart.

The dryer consists of two parallel brick tunnels each 4 by 6 ft. in cross-section, inside, and 250 ft. in length. A 30-in. gage track passes through each tunnel and a single return track on the outside serves both tunnels. The tunnel tracks and the return track are connected through three turn tables at each end of the tunnels. One tunnel is equipped with an endless chain car-haul, running its entire length between the rails, the chain carries dogs which engage each car. The other tunnel has a friction winch and cable for advancing the cars. The tunnels are closed by steel doors at both ends.

The two tunnels are operated in parallel. The cars advance against a stream of hot air forced into both tunnels simultaneously at the car outlet end. The air is supplied by a single 48-in. Sirocco fan, which draws air from the outside through a spray washer and forces it through two banks of heating coils to the ducts entering the tunnels. The coils are heated by steam at 90 lb. pressure.

The air enters the car outlet end of the tunnel at 120° C. and leaves the opposite end at 60° C. and approximately 70 per cent. relative humidity. Recording thermometers and hygrometers allow good control of dryer conditions. The white lead pulp enters the dryer at 45 per cent. moisture and is discharged at approximately 0.20 per cent. The allowable limit of moisture content is 0.50 per cent. Passage through the dryer requires about 16 hours.

The dried product is discharged by removing the trays by hand and dumping the white lead into the boot of a belt-and-bucket elevator, which delivers it to a wooden bin of 20 tons capacity, for storage. Each car is sampled before dumping, the appearance and "feel" of the dried white lead is a reliable indication of its moisture content. This is checked by a laboratory determination of moisture for each shift.

At the dryer discharge, the material closely resembles lump starch in appearance and texture; it is "bone dry" and falls to a fine powder under

slight pressure of the fingers. The preparation of this material for barrelling involves merely the crushing of these soft lumps. No true grinding, in the sense of the reduction of the size of particle, is required. The particle size is determined in the initial formation of the product in the cell and remains unchanged through subsequent operations.

As stated, the equipment for handling the product in the present plant has been selected for the quality of the work done and the control afforded, and does not represent the most efficient and economical equipment for the purpose. This is particularly true of the drying operation. The tunnel dryer, using trucks and trays, is a standard machine and affords a complete control of conditions affecting the final product. The product is, therefore, safe and a good opportunity is given for studying the peculiar requirements of the material being handled; however, the tunnel using a single pass of air heated with high pressure steam has a high operating and repair cost and a very low overall operating efficiency. The drying characteristics of electrolytic white lead are now understood and extensions of the plant will include continuous automatic drying equipment adapted to the material.

PULVERIZING AND BARRELING

From the storage bin, the dried white lead is delivered to a three roller Raymond mill with standard air separation system, this delivers an air-floated product, entirely free from lumps, for packing. The pulverized product is delivered to a standard heavy-duty barrel packer and packed in barrels for shipment. The standard shipping package is a wooden flour barrel with tongue and groove staves, four wood and four wire hoops. No liner is used. This barrel holds 600 lb. of dry white lead.

ANODE SLIME PRODUCTION AND RECOVERY

Lead of practically any composition may be used for anodes in this process without affecting the purity or quality of the white lead produced. The metals, other than lead, in the anode are recovered in the form of a slime, which adheres to the anode surface and is recovered by removing the anodes at regular intervals and scouring the surface clean. The frequency of removal is determined by the amount of slime-forming material present, and is based on two considerations—the increase of internal resistance of the cell and consequent power loss with accumulation of slime, and the insoluble-anode action of a slime-coated anode, resulting in the decomposition of sodium acetate. The present plant uses the desilverized common lead regularly produced by the International Lead Refining Co. The average composition is as follows:

Silver, ounce.....	0.29	Copper, per cent.....	0.0004
Lead, per cent.....	99.87	Zinc, per cent.....	0.0029
Antimony, per cent.....	0.012	Bismuth, per cent.....	0.111
Arsenic, per cent.....	0.0005		

The slime produced from anodes of this lead has the following composition:

Silver, ounce.....	33.3	Copper, per cent.....	0.06
Lead, per cent.....	66.17	Zinc, per cent.....	0.40
Antimony, per cent.....	1.86	Bismuth, per cent.....	10.35
Arsenic, per cent.....	0.08		

The lead in the slime is present largely in the form of white lead, held mechanically by the slime, the remainder as metallic sponge, scoured from the surface of the anode by the washing operation.

An interesting point is the presence of a small amount of lead sulfate in the slime, though none appears in the white lead. The only source of sulfur in the process is from traces of SO_2 in the CO_2 used for carbonation of the catholyte. This appears to migrate to the anode, where it is oxidized, precipitated and removed with the slime, thus protecting the white lead from contamination. All other metals in the slime appear to be in the form of metallic sponge. The slime is dark gray, extremely fine, and adheres to the anode as a smooth coating. The rate of production of slime is approximately 250 lb. per 24 hr.

Each set of anodes is removed and washed at 12-hr. intervals. The eighteen anodes are picked up, as shown in Fig. 4, and lowered into a wash tank through a grid of spray pipes and stiff bristle brushes, which scour and wash the anode surface bright and clean. The water used for this purpose is the discard from the Moore filter, which contains traces of sodium salts and serves to precipitate any soluble lead in the slime. The slime from all wash tanks is pumped to settling tanks, from which it is removed periodically and disposed of for its lead, silver, and bismuth content.

The washing operation requires 10 min. per cell, which is time lost, but gives an opportunity for regular inspection of the cell and cathode frames, cleaning of contacts, etc., which helps to keep the cell in uniformly good operating condition.

ELECTRICAL EQUIPMENT

Electric power is purchased from a local company. All power used at the white lead plant, as well as the refinery and other departments located on the same property, enters on one line and is distributed through the substation at the white lead plant. The incoming power is all transformed from 11,000 to 2200 volts, and a portion is further stepped-down to 440 volts for distribution.

All operating units in the plant have individual motor drive. The dryer fan and Raymond mill are driven by 2200-volt a.c. motors, all other motors are 440-volt, a.c. Monorail hoists in the cell room and at the Moore filter are operated by direct current at 250 volts. Direct current for electrolysis is supplied at 170 volts.

The substation equipment consists of the transformers and switch-board equipment for distribution of all power, the motor-generator set for supplying power to the cells, and a small motor-generator set for furnishing 250-volt direct current to the hoists. The generator for supplying power to the cells is a General Electric type M. P. C., 8-875-514, Form L, designed for 3600 amp. at 240 volts and a speed of 514 r.p.m. This is direct-connected to a General Electric synchronous motor, Type A-T-1, 2200 volts, 328 amp., 60 cycles, 1250 hp. The small motor-generator set consists of a 250-volt, 25-kw., d.c., generator direct connected to a 35 hp. motor, Type KT, 440 volts, 412 amp. Air for cooling the motor generators and transformers is drawn from the outside through a spray washer and cooler and forced down upon the machine through piping suspended from above.

BOILER HOUSE

Steam at 90 lb. pressure for heating the dryer, heating water at the Moore filter and for heating buildings in winter, is supplied by two 60 hp. and one 150-hp. locomotive-type boilers. The 35-hp. boiler used as a producer for carbon dioxide is also connected to the main steam line.

FLOW SHEET AND OPERATING DATA

A general operating flow sheet of the plant is shown in Fig. 11. Miscellaneous operating data are tabulated below:

New anode weight, pounds.....	250.00
Scrap anode weight, pounds....	75.00
Time of corrosion, hours.....	85.00
Cell voltage.....	3.50
Current density, amperes per square foot.....	29.60
Current efficiency, per cent.....	97.0
Anolyte temperature, degrees C.....	40.0
Thickener feed, per cent. solids.....	0.50
Thickened pulp, per cent. solids.....	30.00
Washed filter cake, per cent. solids.....	55.00
Dried product, per cent. moisture.....	0.20
Dryer temperature, maximum, degrees C.....	120.00

CHARACTERISTIC OF PRODUCT

The outstanding characteristics of the white lead produced by the electrolytic process are exceptional purity and uniformity, extreme fineness of grain, and brilliant whiteness.

Basic lead carbonate has the formula $2 \text{PbCO}_3 \cdot \text{Pb(OH)}_2$, representing the following percentage composition.

PbCO_3 , per cent.....	68.90	Total Pb per cent.....	80.14
Pb(OH)_2 , per cent.....	31.10	Total CO_2 , per cent.....	11.35

Normal lead carbonate, hydrate, and basic lead carbonate have distinctly different physical properties; the normal carbonate is crystalline and the hydrate amorphous, while the basic carbonate, though crystalline under the microscope, possesses certain peculiar properties that cause it to work well as a pigment. Both normal lead carbonate and lead hydrate are unsuitable for use as pigments. Commercial white leads contain various mixtures of normal carbonate and hydrate with the basic carbonate, approaching the theoretical composition of basic carbonate as a mean, but varying from it considerably in physical characteristics.

The electrolytic process furnishes an exact control of chemical composition and yields a pure basic carbonate free from contamination by other lead compounds or by other metals contained in the original lead. The soluble salts from the electrolyte are easily removed by washing, and their neutral or alkaline character insures a product free from acidity or soluble lead. The particle size is that obtained by precipitation, and is much finer and more uniform than would be obtainable by grinding.

COLOR

The product is a brilliant white, this is the result of both purity and fineness. This property is of importance in a pigment, not only in yielding a white paint of great beauty but in its effect on other colors with which the pigment is combined in mixed paints.

The control of color of product in the electrolytic process lies almost entirely in simple protection against dirt. The color of the normal electrolytic white lead is very little affected by irregularities in operation, such as would affect the CO_2 content of the product, as both lead hydrate and lead carbonate are white compounds. It is possible, however, under very irregular conditions, such as the complete interruption of circulation in a cell, to form lead oxides, that are highly colored and will throw the entire product "off color." This represents an unusual condition and would be accompanied by other effects still more noticeable.

Extremely small amounts of foreign matter have a noticeable effect on the color and, once in, their removal is practically impossible. Purity of color is a much better indication of freedom from such contamination than any chemical analysis.

The plant includes no operation calculated to remove contamination from the cell-room product. The white lead is protected by proper

selection of the materials with which it comes into contact, and by the covering of all tanks and bins to exclude dust.

A series of samples of the white lead, one representing its entrance to each stage of the operation, is taken every 24 hr. Each sample is compared with a standard and any color irregularity is easily detected and checked.

The final barrelled product is sampled as it is packed. A color analysis is made on each day's production, using the Pfund Colorimeter. A standard is run simultaneously with each sample. This furnishes a complete color record of all production and insures a uniform shipping standard.

HIDING POWER

Due to its extreme fineness and uniformity, electrolytic white lead produces a paint that may be brushed out very thin, forming a film that dries hard and possesses the same opacity and hiding power as much thicker coats of paint made from coarser, less uniform pigments.

These characteristics mark the product, and the process that produces it, as noteworthy advances in a field that constitutes one of the principal industrial applications of lead.

ACKNOWLEDGMENTS

Credit for the development of the process to its present status, and for the solution of many problems of operating detail and design of equipment, is due the entire staff at East Chicago, and particularly to Mr. O. M. Kuchs, manager and Mr. G. E. Johnson, superintendent.

Lead Smelting in Utah

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LEAD smelting has been an important industry in Utah for many years. The first lead smelting was done, over 60 years ago, at the Rollins mine in Beaver County, by burning heaps consisting of alternate layers of wood and high-grade carbonate ore. The lead thus obtained was molded into bullets. With the development of the mines, the problem of cheaper handling of the ore became important. The only outlet for this ore was Swansea or the Atlantic Coast but to ship to either cost \$150 per ton or more for treatment and handling.

From 1864 to 1871, experimenting was done with blast, Scotch hearth, and reverberatory furnaces, with the blast furnace surviving as the standard plant. The first crude furnaces were circular or hexagonal in shape, and were made of adobe and stone, which quickly burned out. They were small, about $2\frac{1}{2}$ ft. in diameter, and smelted from 3 to 10 tons in 24 hr. The metal had to be tapped from the bottom of the crucible, necessitating a shut down of the furnace during this process. This procedure caused salamanders to form around the tap hole when the furnace was started again, which frequently resulted in freezing. The campaign lasted until a tap of bullion was made. The first successful plant of the crude stone type was operated in 1870.

From 1870 to 1872, there was a smelter building craze in the state. During that period, about 20 furnaces were built, chiefly near the mines, and their operation was limited and sporadic. The work was then placed in the hands of trained metallurgists, who standardized on the rectangular form of furnace. In 1871, Daggett, at the Winnamuck mine in Bingham, installed water-jackets around the smelting zone of the furnaces. These furnaces were circular; the diameter at the tuyere line was 3 ft. 6 in. and at the charge floor 5 ft. 3 in. The height from tuyere line to charge floor was 14 ft., height of tuyere line above top of crucible was 3 ft. 8 in. Furnace capacity was about 14 tons per day, with a campaign of about 16 days. Cost of smelting was about \$44 per ton. The ores making the

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charge mixture were bedded on the feed floor of the furnace, as was the common practice at that time. The siphon lead well was invented almost simultaneously at Eureka, Nev., and at the Sultana smelter in American Fork canyon; credit for the invention has gone to Arents at the Eureka smelter. This well permitted a continuous furnace operation.

Although many oxidized ores high in iron were treated, these isolated plants had to get some hematite, for flux, from Wyoming, at a cost of about \$25 a ton. The fuel was entirely charcoal, made by burning available woods; this resulted in so poor a quality that some plants secured their supply of fuel from Sierra Nevada burners. By either plan, the fuel cost from \$22 to \$25 a ton.

Centralization of operations started at this time with the building, in 1872 at Murray, of the Germania plant; at first this was only a refinery, the lead stacks being added two years later. Other custom plants were also in operation in the Salt Lake valley. The Germania plant consisted of one reverberatory furnace for roasting ores and matte or slagging flue dust, three shaft smelting furnaces, three softening and refining furnaces, seven pots for desilverization of lead by zinc, six zinc distillation furnaces, and three English cupel furnaces; it was rated among the most important metallurgical plants in the West.

Some of the plants made matte, others did not. Where matte was made, it was either heap-roasted or roasted in hand-rabbed reverberatory furnaces. Most of the roasting showed a slight loss in lead and but slight lowering of sulfur. Flues from the roasting furnaces were divided into compartments to effect a dust saving; the compartments had openings through which the dust could be hoed. Here also was the forerunner of the baghouse, as some of the plants suspended battens or filters of cotton or wool cloth in the flue compartments.

In the next few years, larger plants were installed. At one of the valley custom plants, furnaces built in 1877 were 3 by 3 ft. 6 in. at tuyeres and 34 ft. high, and had a capacity of 35 to 40 tons of smelting mixture in 24 hr. By this time Pennsylvania coke was largely being used, it being a better fuel at about the same cost as charcoal. The length of a run was about 4 months. The charge varied from 13 to 22 per cent. lead, the slag contained from 40 to 45 per cent. ferrous oxide, from 28 to 33 per cent. silica, and 15 to 20 per cent. lime. Matte, flue dust, and speiss were roasted either in heaps or in reverberatory roasting furnaces, and retreated.

Practice remained virtually unchanged until the late 80's, when increasing amounts of sulfide ores were mined. For some years during the late 80's a large part of the mine output was shipped out of the state for treatment. This brought on an intensive study of the roasting problem. Briquetting of fine material came into practice. The Bruckner, or cylinder, type of roaster came into common use, it being supplemented

by heap or reverberatory roasting. A number of mechanical roasters were tried during this period.

By 1900, when new and larger plants were built, the Huntington and Heberlein pots using air blast were used for roasting and sintering. Adoption of mechanical equipment throughout the smelting plants was established to a greater degree to permit cheaper handling of larger tonnages.

With the increase in fine materials and the handling of greater quantities of sulfide ores, the fume problem was presented and in the next few years after 1902 the smoke problem became more acute. That problem was met by the baghouse, of which the first was built in 1906 and put in operation the next year. Diffusion of gases through use of higher stacks was also started. Briquetting continued the practice to care for the fine material.

The last period, from 1910 to the present, saw the development of Dwight-Lloyd machines for roasting and sintering, which greatly bettered roasting practice, making a porous sinter for the blast furnaces. During this period, also, came the Cottrell electrical precipitator for the recovery of flue dust and fume under conditions where baghouses were impractical. In the handling of ores came the bin system and the use of electrically operated, drop-bottom, charge cars drawing the various constituents of the charge from different bins.

PRESENT DAY SMELTING PLANTS

There are at present three lead-smelting plants in Utah, all within a radius of 35 miles of Salt Lake City.

American Smelting & Refining Co.

The largest lead-smelting plant operated by this company is located at Murray, Utah, 7 miles south of Salt Lake City. Operations were started in August, 1901. The roasting and smelting equipment consists of seven standard Dwight-Lloyd sintering machines, six Wedge and five Godfrey roasting furnaces, and eight blast furnaces with lead drossing plant. The plant is also equipped with adequate, modern flue systems, baghouses, and Cottrell treaters for recovery of flue dust and fume.

United States Smelting, Refining & Mining Co.

This company's plant is located at Midvale, Utah, 12 miles south of Salt Lake City. Operations were started in November, 1902, when one copper furnace was blown in. The first lead furnace was blown in the latter part of January, 1905. The roasting and smelting equipment

consists of six standard Dwight-Lloyd sintering machines, five Wedge and one McDougall roasting furnaces, and seven blast furnaces, with lead drossing plant. In addition, there are three Brunton arsenic furnaces and two arsenic refining furnaces. The plant is equipped with large flue system and baghouses for recovery of fume and flue dust.

International Smelting Co.

The lead plant operated by this company is located near the Salt Lake-Los Angeles line of the Union Pacific R.R., 35 miles southwest of Salt Lake City. It is connected to the Union Pacific by 6 miles of its own track. This plant was blown in as a copper reverberatory smelter in August, 1910. Lead-smelting operations were started in February, 1912. The lead-roasting and smelting equipment consists of ten standard Dwight-Lloyd sintering machines, eleven McDougall roasting furnaces, and five blast furnaces, with lead drossing plant. Ample flue systems, baghouses and Cottrell precipitators are provided for fume and flue dust recovery.

PREROASTING

Types, Sizes, and Capacities of Preroasters

Preroasting is being done in Utah lead smelters in McDougall, Wedge, and Godfrey roasting furnaces. The McDougall roasters are six-hearth, 16-ft. furnaces treating 40 to 80 tons of wet feed per 24 hr. and eliminating sulfur from 32 to 35 per cent. in the feed, to 11 to 17.5 per cent. in the calcine, the greater sulfur elimination accompanying the lower tonnage. The Wedge roasters are eight-hearth 21-ft. furnaces with the top hearth as a drying hearth. These furnaces treat 80-115 tons wet feed per 24 hr. with about the same sulfur elimination as in the McDougall roasters. The Godfrey furnaces are single-hearth, 25-ft. diameter roasters. The hearth revolves and the rabbles are stationary. The furnaces treat 20-25 tons of feed per day. The sulfur elimination is from 33 per cent. sulfur in the feed to 12 per cent. sulfur in the calcine.

The rabble arms in McDougall furnaces are water-cooled. The Wedge furnace arms are water-cooled, except in two instances where air is used for cooling. The air cooling used in the later type Wedge furnaces is working very satisfactorily.

Making Up Preroasting Charges

The methods of making up the charge for preroasting furnaces are very much the same. The various ores and concentrates are delivered from storage bins to a conveyor, in the proportions in which they are to be used. This conveyor delivers to the roaster-feed hopper or bin. The only mixing of the charge takes place as it is delivered from the conveyor to the hopper and as it works down through the hopper. The proportions

of table or jig concentrates, flotation concentrates, crude sulfide ores, and matte are variable and will change from time to time with the ore supply for each plant. One plant is treating a mixture of 30 per cent. flotation concentrates, 30 per cent. table concentrates, and 40 per cent. crude sulfide ore. Another plant is treating a mixture of 50 per cent. table concentrates and 50 per cent. crude sulfide ore. The third plant is treating a mixture of 60 per cent. flotation concentrates, 20 per cent. table concentrates, and 20 per cent. crude sulfide ore or matte. The crude sulfide ore or matte treated in a preroasting furnace must be crushed fine, in order to eliminate sulfur to any great extent. Two of the plants have special grinding machinery, with vibrating screens returning oversize to the rolls, for preparing sulfide ore for roasting. The maximum size from these mills is $\frac{1}{4}$ in., the other plant grinds through $\frac{1}{2}$ -in. revolving "trommel" screens.

Feeding Devices

The feeding device on the McDougall roasters consists of plungers moving on a feed plate directly across the bottom of the feed hopper, forcing a definite amount of feed out of gate openings at the bottom of the hopper. The plungers are driven, by an eccentric, direct from the furnace column. The gate openings at the hopper bottom and the plunger throw are adjustable, giving fairly close regulation of feed. The feed drops on to the first hearth and is moved on through by the rabblers. The Wedge furnaces are equipped with belt feeders driven by a worm and gear independent of the furnace drive, except in one case. This one furnace has two disk feed tables at opposite sides of the furnace; these tables are turned by each rabble arm as it goes by. The amount of charge fed is regulated by the depth of charge carried on the feed table from the feed hopper. The feed on all the Wedge furnaces drops on to the top, or drying, hearth and is carried through the furnace by the rabblers.

The charge of the Godfrey furnaces is delivered from a screw conveyor connected to a variable-speed drive; this allows a very positive regulation of feed to the hearth.

Sulfur Elimination and Degree of Calcination

The sulfur elimination varies materially with the amount of feed treated in a given time. On the McDougall roasters, with about 40 tons of feed per 24 hr. containing 33-35 per cent. sulfur, the calcine will contain 10.5 to 11.5 per cent. sulfur. If, however, the amount of feed treated in the 24 hr. is reduced to about 30-32 tons, the calcine produced will contain 7-8 per cent. sulfur. On the other hand, if the feed treated is raised to 70-80 tons per 24 hr., the calcine produced will contain from 16-17.5 per cent. sulfur. This same relationship holds true on Wedge roasters. The degree of calcination on McDougall roasters making a

low sulfur calcine will average about 1.13 tons of feed into 1.00 of calcine. Degree of calcination on Wedge and Godfrey roasters will average about the same. The sulfur in the charge is usually sufficient to furnish the necessary heat for roasting in McDougall and Wedge furnaces. If a large tonnage, such as is treated at one plant, goes through a furnace, additional heat is necessary to eliminate sulfur. One plant, treating 80 tons of feed through a McDougall furnace, fires on three or four hearths, using one or two oil burners on each hearth. Another plant, using McDougall furnaces, has fireboxes for coal firing on the third hearth but uses them only occasionally. The third plant has oil burners on second and third hearths that are used at times. The necessity for this extra firing is dependent on the amount of sulfur in the charge, physical characteristics of the charge, and the sulfur elimination required. In the case of Godfrey furnaces, considerable fuel must be used as the charge is in the furnace for a short time only; 7-8 gal. of oil are used per ton of charge on these furnaces.

Operation and Difficulties

The main difficulty encountered in the preroasting operation is the upkeep of the furnaces. The burning of the sulfur from these lead ores and concentrates produces a great deal of heat. The larger the amount of flotation concentrates, the more heat liberated on the early roasting hearths. This tends to fuse the charge into a solid mass and, if this does happen, the rabblers will be unable to plow through the bed and the furnace will stop. This always means a large amount of barring on the hearths. The rabblers themselves burn very badly in a deep bed of hot charge and require frequent changing. The rabblers, or rakes, on Wedge roasters are larger and heavier than on McDougall furnaces and consequently have longer life. The faster the rabble arms move, the less material there is on each hearth for a given furnace tonnage. A certain time must be allowed, however, for the heating up of the charge and the burning off of the sulfur. On McDougall roasters, the most efficient speed for the rabble arms has been found to be from 58 to 60 sec. for one complete revolution. On the Wedge furnaces, the time for one revolution varies from 150 to 226 sec. If the rabblers travel slower than this, the bed is too deep to allow thorough exposure to the air for burning; also, the deep bed burns the rabblers off badly and tends to fuse more readily. If higher speed is used, the sulfur elimination is not as great.

Matte Roasting

One of the Utah plants is preroasting blast-furnace matte in a Wedge roaster for matte concentrating runs at the blast furnaces. This matte is ground through $\frac{1}{4}$ -in. screens and is handled through the roasting furnace in exactly the same way as the ore mixture on the other roasters. Some

additional heat is required at times, but if the matte is ground fine enough extra heat is seldom required. This furnace roasts matte from 22 per cent. sulfur down to 17 per cent. sulfur, and is doing splendid work; its output is about 75 tons of matte per furnace day.

Handling of Calcine

All the Wedge furnaces and the McDougall roaster used at one plant have water sprays at the end of one rabble arm on the last hearth. These sprays use the cooling water, where the furnace is water-cooled, and have a separate water connection, where air cooling is used. As the rabble travels around the hearth, the calcine is sprayed and rabbled over to the drop hole. When it finally drops off the last hearth it is cool and contains about 5 per cent. H_2O . Some of the Wedge furnaces have a revolving disk table below the last hearth, where further wetting can be done before delivering calcine to storage bins. This procedure puts the calcine in good condition for use at the sintering machines. At the other plant using McDougall roasters, the calcine is discharged from the last hearth into a storage hopper from which it is drawn hot into railroad cars. From the cars, the calcine is dumped to sinter plant mixing bins. Great care must be taken when dumping this material into bins to see that no wet material is mixed with it, as this will cause explosions with the hot calcine. The calcine from the Godfrey furnaces is moistened as it leaves the moving hearth to the hopper; about the same moisture is carried in this calcine as in the Wedge and McDougall calcine.

SINTERING

The sintering machines used at the three Utah plants are all standard Dwight-Lloyd, 42 by 264 in. They have a capacity of from 100 tons to 225 tons per machine-day, according to the speed at which they are operated and the nature of the charge; the pallet speed varies from 15 to 33 in. per min. The pallet travels over a 22-ft. suction, or wind, box, in which a suction of 8 to 10 in. of water is maintained by a fan. Each machine is driven separately and has its own fan and motor. At one of the plants 75-hp. motors are used to drive the fans; at the other two plants 50-hp. motors are used. The machines are driven by variable-speed motors, which allow variations in the pallet speed.

Stewart grates are used at all the plants. This grate consists of three loose, or movable, grates and four that are held tight in the pallet. As the pallet is dumped at the end of the machine, the movable sections tip a little, thus cleaning the grate. This is an important feature, as considerable difficulty was encountered keeping open the old type, straight slot grate.

Mechanical Feeders

The mechanical feeders at the machines used at the different plants all aim at the same result, which is to deliver the charge on to the grate

in such a way that the coarse material rolls down to the grate first and the finer material falls upon that. This bedding on the grate keeps the fines from dropping through and also keeps the lower part of the charge more porous, allowing the air to be drawn down through the bed more readily. One plant has two types of feeders in use. One is a belt feeder with a variable-speed cone drive, which delivers the feed from the hopper on to a feed plate, the face of which is set at about 15° from vertical and is shaped like a segment of a truncated cone. The charge delivered from the belt conveyor drops on to the top of this conical plate and, in rolling down its face, is distributed the full width of the pallet. As the feed leaves this feed plate, it strikes against another, vertical plate, set a few inches above the grates, which causes the coarser material to rebound from it farther than the finer material. This gives the desired bedding and distribution of the charge on the grates. The vertical plate acts as a scraper that may be raised or lowered, thus regulating the depth of the bed of ore on the pallet. The other feeder used at this plant is the same in every way except the belt feeder. It has a revolving disk feeder directly under the feed hopper. As this disk revolves, the charge is drawn out from the hopper on to its surface. A scraper is located just over the center of the conical feed plate, which scrapes the charge off the disk. The amount delivered by the revolving disk is regulated by the depth to which the scraper cuts the bed carried by it.

Another plant uses revolving disk feeders delivering direct to a feed plate, which is the same as described. The third plant is equipped with belt feeders driven by variable-speed cones, which deliver from the feed hoppers to small barrel-type mixers; one at each machine. The discharge from each of these mixers goes into an oscillating chute, which distributes the charge very evenly over the full width of the pallet.

Composition and Preparation of Charge

The various materials making up the sintering charge are mixed in the desired proportions in much the same way at all three plants. The individual constituents, such as preroast, oxide fines, crude sulfide ores, etc., are stored in separate bins from which they are drawn in definite proportions, by belt or disk feeders, to a conveyor that delivers the mixture to the machine feed hoppers. The amount of each material delivered to the conveyor is regulated by the gate opening from the bin to the feeder. The belt feeder is better than a disk feeder for fine, wet material such as concentrates, but the disk feeder works very satisfactorily on fairly dry material that does not readily pack. One plant delivers the charge from the conveyor to a pan mixer, where it is mixed by rotating rabblers before it is discharged on to another conveyor, which carries it to the machine-feed hoppers. Another plant uses no mixer, but the charge is transferred from one belt to another twice, thus giving considerable

mixing. The third plant has small barrel-type mixers for each machine feed hopper.

The charge varies with the ore supply at each of the smelters. The proportion of crude sulfide ore, oxidized fines, preroasting material and concentrates is determined by the character and analyses of the ore supply. All the material must be finely ground in order to eliminate sulfur during the sintering process. The general opinion seems to be that the proportion of silica to iron in the charge has very little to do with the grade of sinter produced or with the sulfur elimination. One plant, where there is much flotation concentrate on the charge, finds that crushed lime rock helps to bed the grates properly, thus aiding sulfur elimination. The other two plants do not use lime rock on the sintering charge. Material which is quite readily fused, such as matte or slag, helps materially to make a hard, porous sinter. Slag or matte is being used at two of the smelters, but not by the third. Crude sulfide ores containing considerable pyrite furnish very good fuel and tend to carry the sintering action down through the bed after it is ignited.

In the three plants the sintering charge is made up as follows:

	PER CENT.	PER CENT.	PER CENT.
Sinter fines.....	17	7-8	15
Preroaster material.....	26	75	40
Crude sulfide ore.....	5	10	5
Table concentrates.....	5	7-8	
Oxide fines.....	12		32
Flotation concentrates.....	18		
Flue dust.....	5		
Lime rock.....	4		

The preparation of the charge to the sintering machine is of utmost importance. In the first place, the various materials must be used in definite proportions and the proportions of silica, iron, and lime in the resultant mix must be constant. The sulfur in the charge must remain practically constant in order to maintain consistent operation in sintering. The percentage of moisture in the charge must be held within very narrow limits. Variation in these two items will make marked irregularities in the sinter produced. Too much sulfur in the charge will cause the top of the bed to fuse as it passes under the igniting flame; then when the pallet has moved from under the burner, the burning or sintering cannot continue downwards through the charge to the grates because sufficient air is not drawn through. If the sulfur is too low there is not enough fuel present to carry the sintering on through the bed. The result in either case is poor sinter and poor sulfur elimination. The same conditions hold true with regard to moisture. If the charge is too wet, the

LEAD SMELTING IN UTAH

sulfur will not ignite under the burner and the sintering is not even started; if it is too dry, the sulfur ignites under the burner but does not continue to burn after the pallet has moved from under the burner. Different charges require different amounts of moisture to make the best sinter. One plant finds 8 per cent. moisture best for its charge, another finds 9-10 per cent. best, and the third finds 7-8 per cent. best. The sulfur in the charge averages from about 11.5 to 13 per cent.

Two very important features in proper charging are the bedding of the charge on the grates and the uniformity of the charge at all parts of the pallet. The ideal practice is to feed the charge exactly as fast as the pallet bed removes it; the less feed that must be scraped back by the scraper plate, and still maintain a bed of uniform thickness, the better. A building up of the charge at the scraper plate tends to pack the bed, making it more difficult to sinter the charge properly. If much of the coarse material goes to one side of the pallet and the fines to the other, neither part makes sinter, as the air does not penetrate the fine part and the coarse part does not contain enough sulfur for its sintering. The depth of bed carried may be varied by raising or lowering the scraper plate; this depth is 4 and 5 in. at different plants; the depth of the pallet itself is 4 inches.

Firing

The sintering charge is ignited with oil burners at all three of the plants; using high-pressure burners with engine distillate or gashouse oil of about 36-38° B_é. The oil is fed by air pressure to the burner and the air is supplied under 90 lb. pressure. One of the plants is trying out a Hauck low-pressure burner (35 oz. air) with good results. The burner is placed at one edge of the pallet and the flame is directed across the pallet. The flame must carry entirely across the pallet in order to give proper ignition to the charge. A muffle hung over the top of the bed, directly in line with the burner, confines the heat to the top of the charge, thus protecting the operator. The muffle is made of V-shaped cast-iron blocks at one plant and of brick at another; the third plant uses a water-jacketed brick-lined muffle. Oil consumption at the different plants is between 0.45 and 0.60 gal. per ton of charge.

Sinter Fines

Each of the three plants is equipped with grizzlies at the discharge end of sintering machines to screen out the fines. This fine material is higher in sulfur than the coarse sinter and is returned in the feed to be resintered. One plant sends these sinter fines on an armored conveyor directly back to the feed conveyor to the machines. Another plant delivers them, by means of screw conveyors, to railroad cars, which in turn are dumped to one of the feed bins above the mixing floor. The

third plant discharges these fines to small cars; they are then dumped into the mixing bins thence back as part of the charge. The amount of fines produced varies a good deal with the quality of sinter being produced and with the spacing of the grizzlies. One plant produces about 17.0 per cent. fines; another plant 7-8 per cent., the third about 15 per cent. The grizzly spacing, respectively, for these percentages of fines is $\frac{3}{8}$, $\frac{3}{4}$ and $\frac{7}{8}$ inch.

Sulfur-elimination Tonnages

The percentages of sulfur in the feed to the sintering machines at the three plants is much the same; it ranges between 11.5 and 13.0 per cent. The sinter produced ranges from 3.5 to 4.5 per cent. sulfur. The degree of sintering is quite constant; averaging about 1.115 tons of dry feed to 1.000 ton of sinter (feed not including sinter cleanings). The rate of travel of pallets over the wind boxes, the depth and character of charge on the pallets, and the amount of effective draft are all important factors in sulfur elimination.

Pallet speed and depth of charge on pallets are the determining factors in tonnages treated. The Utah plants are using a pallet speed of 19 to 26 in. per min., which with a depth of bed of 4 or 5 in. will produce 110 to 125 tons of sinter per machine per 24 hours.

Handling of Sinter

The sinter at all three plants is delivered from the ends of the sintering machines, over grizzlies, direct to railroad cars. From the cars, the sinter is dumped to storage bins for use at the blast furnaces. At two of the plants, the sinter is sprayed with water as it is loaded into cars; at the other plant, the sinter is sprayed in the storage bins.

The quality of sinter desired for the blast furnaces is porous, hard, and free from fines. The size of the sinter is not so important as long as the amount under 1 in. is small. There is bound to be considerable breaking up of the sinter in dropping from the machines to the cars and in dumping from cars to bins; first-class sinter will not produce any great amount of fines from handling.

Acid in Gases

The gases produced by the sintering operation contain small amounts of SO_3 and considerable moisture. If this gas becomes sufficiently cool to permit condensation of moisture, sulfuric acid is produced which will quickly destroy any woolen bags in a baghouse. One of the plants, which handles this gas through a baghouse, introduces powdered lime into the gases before entering the baghouse to neutralize this acid. The other two plants handle this gas in Cottrell treaters and do not neutralize the acid.

Elemental Sulfur

In the process of sintering, where considerable amounts of pyrite are used on the charge, elemental sulfur is distilled off from the charge and condenses in the flues, treater, or baghouse. The presence of elemental sulfur in comparatively large amounts, or in smaller amounts mixed with finely divided carbon, has been the cause of very destructive fires and explosions. The amount of elemental sulfur produced seems to be quite definitely proportional to the amount of crude pyrite on the sinter charge.

BLAST-FURNACE SMELTING

Furnaces

Lead blast-furnace smelting at the three Utah plants is much the same insofar as general practice is concerned. The furnaces are all quite similar in general design. They are rectangular and vary in width at the tuyere line from 48 to about 54 in. and in length from 160 to 180 in., the height from tuyere line to feed floor is between 24 and 25 ft. At two of these plants, the furnaces are provided with but a single tier of water-jackets, about 6 ft. high above the top of the crucible. At the third plant a double tier of water-jackets is used on all furnaces, thus jacketing the furnace at sides and ends for a height of about 15 ft. above the top of the crucible. This double tier of water-jackets permits much easier cleaning of furnace stacks than is possible where brick walls are used above a single tier of jackets. Widths of jackets used vary from about 32 to 60 in. Ten and twelve 4-in. diameter tuyeres are used on each side of these furnaces, the number varying at different plants. All furnaces are provided with Arents siphon tap for removal of lead, on one side of the furnace, near the front or tapping end.

The furnaces at the three plants are of similar construction on top. The gases from the furnaces are removed, just below the charge floor, at the back end of the furnace. The charge cars are run over the tops of the furnaces and the charge dropped through drop-door bottoms, over the entire length of the furnace at one time. When not being charged, the furnace tops are covered by drop or slide doors, so that but little smoke or dust gets out on to the charge floor. The charge cars from which the charges are dropped into the furnaces are quite similar, in many respects, at all three plants. At two of the plants, these cars are electrically driven; and at the third plant the charge car is carried on top of an electrically driven, traveling, steel framework on the charge floor. The drop-door bottoms are full length of the car, one door on each side; they are dropped by means of a latch release and are closed by hand-operated devices; either wind-up wheel and chains or levers and counterweights. The charge drops on to a steel "spreader" suspended within the stack of the furnace about 1 to 3 ft. below the feed-floor level. This spreader aids in a proper distribution of the charge, as

regards coarse and fines, in the furnace and breaks its fall so as to prevent excessive packing when charges are fine.

Charges

The blast-furnace charges at all Utah plants consist, to a large extent (55 to 75 per cent.), of sinter, made on Dwight-Lloyd machines. An excellent quality of lime rock from nearby quarries forms from about 6 to 20 per cent. or so of the total charge. Coarse lead-silver ores, low in sulfur content, usually form an important constituent of these charges. Iron flux is obtained in several forms—low-grade lead-silver ores high in iron or manganese, barren iron flux, converter slags high in iron, and scrap iron of all kinds and descriptions. The remainder of the charge generally consists of secondaries, such as flue dust and baghouse fume, briquetted or loose, and furnace cleanings. To each charge is added the necessary amount (usually 11–13 per cent.) of coarse Utah coke. The weight of charge is 7500, 8000 and 9000 lb., respectively, at these plants; the coke is additional and is expressed as a percentage of this weight.

In recent years the amount of lead present in blast-furnace charges has been from 10 to 25 per cent. of the total charge less returned secondaries; usually this figure lies between 15 and 20 per cent.

Charge Weighing

The greatest care and accuracy are necessary in making up lead blast-furnace charges; each constituent of the charges must be carefully weighed. Charges are made up in somewhat different ways at each of the Utah smelters. At two of the plants, the "spreading bed" system is used for all direct smelting ores, but the method of handling the charge to the furnaces differs widely. At one plant, the direct smelting ores and settler barrings are bedded in wooden bins, each holding about 600–700 tons of charge. These bins have flat bottoms with eight feed hoppers built into the bottom along the longitudinal center line. Each hopper under these spreading-bed bins is provided with a mechanically operated arc gate. Sinter, lime rock, coke, etc., are kept in similar bins, which are equipped with short belt feeders under the hoppers, using two belts each 36 in. wide. The forward, or driving, pulley on the feeder is attached to a large gear wheel, which meshes with a pinion on a driving mechanism on a weighing charge car, which is run underneath the hoppers. The arc gates under the spreading-bed bins are also operated by the driving mechanism on this charge car. By these means, the ores and other constituents of the charge are delivered into the charge car, which is equipped with scales, upon which the carbody rests. There are ten beams on the scales, so that ten weights of materials may be obtained. The motorman on the charge car controls the operations of the belt

feeders and arc gates by means of the driving mechanism on the car. The desired weight of any material is shown by a finger-like indicator, which may be used in turn with each of the ten beams on the car scales. The charge car passes from one hopper to another, drawing off desired weights of each constituent until the charge is completely made up. The charge is then transferred, through a baffled opening between the rails of the track on which this weigh car runs, into another electrically driven charge car, spotted beneath, which carries this charge to the furnace top where it is dumped.

At another plant, the spreading beds are large, wooden-side enclosures with flat concrete bottoms, built on the ground. There are three large beds, holding from 2000 to 2800 tons each, and seven small ones, with a capacity of 800 to 1000 tons each. Sinter, lime rock, coke, etc., are kept in wooden bins with elevated, hoppers bottoms. The three hoppers in the bottom of each bin are provided with hand-operated arc gates. The charge from the spreading beds is hand-shoveled into steel buggies and the charge from various bins is drawn through the arc gates into other buggies. These buggies are small, holding about 1 ton of sinter and $1\frac{1}{2}$ ton of bedded ores when filled. Trains of from two to six buggies are handled by Fordson tractors between the spreading beds, bins, scales, and dumping pocket to the charge car. An average of twelve buggies are used in making up the usual blast-furnace charge. The men who make up the charges know what weights of various materials are wanted and estimate remarkably closely the correct weight put into each buggy. From the beds or bins, a train of buggies is taken to platform scales where each buggy is separately weighed. If too much of one material is in a certain buggy, the amount of overweight is shoveled out while the buggy is on the scales and is thrown into a small bin for that material nearby. If there is an underweight in a buggy, the deficiency is made up by shoveling from one of the small bins near the scales. All of this work is done rapidly by experienced men. As soon as the correct weight of material is in a buggy, this buggy is moved by hand to one of the two dumping pockets, a short distance from the scales, where it is dumped. The bottom of each dumping pocket opens on to a pan conveyor feeder, which discharges into a charge car beneath. As each buggy full of charge is being removed from a dumping pocket by the feeder, the charge car is moved forward and backwards so that the charge is distributed from front to back of the car. After all of the constituents of the charge have been spread into the charge car, the car is hauled up an incline, by a hoist and cable, to the blast-furnace feed floor about 30 ft. above. Here it is taken by an electrically operated traveling carrier frame to the proper position for dumping over any one of the furnaces. Two charge cars are in use at one time, one being loaded while the other is being dumped.

At the third plant, each constituent of each charge is weighed directly into the charge car by means of scale hoppers suspended under steel blast-furnace bins; in other words, each charge is bedded in the car as the constituents are weighed in, one on top of the other. As the charge is being dropped from the scale hoppers, the car is so moved along the track underneath as to spread each material over the length of the car in the manner ordered by the furnace feeder. In this way, a charge is made up to suit the conditions in the particular furnace into which it is to be dropped. The coke also is weighed into the charge cars. For a custom lead smelter handling many small lots of greatly varying ores, a system of charge weighing using a weighing charge car or scale hoppers under the bins is very flexible and efficient.

Furnace Operation

The height of ore column above the tuyere line varies from about 11 to 17 ft. for different conditions of charge; the blast pressure varies from about 32 to 40 oz. Generally, when a fairly coarse charge is available, an ore column about 14 to 16 ft. deep and a blast pressure of about 35 to 38 oz. seem to give best results. This seems to be true for furnaces with a width at tuyeres of 48 in. as well as for the wider ones. The narrower furnaces (48 in.) will smelt an average of about 240 tons of ordinary charge per 24 hr., while the wider ones (54 in.) will smelt about 260 tons. The matter of furnace speed is, of course, extremely variable; it depends on the physical character and chemical analysis of the charge being treated, the amount of coke required to hold proper reduction in the furnace, the analysis of the desired slag, etc. With a coarse charge of desirable chemical analysis, requiring a relatively low percentage of coke and permitting the making of a hot and easy running slag, the narrower furnaces will easily smelt an average of 255 to 260 tons per day and the wider ones an average of 280 tons per day for long periods.

Slag and Matte Handling

At the three Utah plants, double settling for separating matte and slag is practiced. Most of the matte is settled out in the first settler; the matte is tapped out of this settler into pans and pots. At one plant, it is possible to tap matte from the second settler as well as the first, thus increasing the length of life of this settler; at the other plants, second settlers are changed every 24 hr. and very little matte gets into them. All the slag, after passing the second settler, is thrown over the dump. Slag pots vary in capacity from 3 to 7 tons; they are drawn by electric and small locomotives.

Blast-furnace matte is handled differently at each plant. At one plant, the first matte, containing about 10 per cent. copper and 9 to 10

per cent. lead, is cast into pans, slightly cooled and broken up, by water sprays, in railroad cars. Most of this matte is shipped to another Utah lead smelter, where there is a converting plant; a small part of it is returned to the Dwight-Lloyd charge. At another smelter, the first matte is cast, cooled, and broken up as just described and then is fine crushed, roasted, and retreated in a blast furnace with siliceous ore and lime rock, making a matte concentration run. In this way, a higher grade copper matte (about 40 per cent. Cu) is made; this matte is shipped to the converting plant at a copper smelter in the state. At the third smelter, the first matte containing 18-25 per cent. copper is handled hot into 96 by 150 in. horizontal, barrel-type converters, where it is blown to a mixture of white metal and magnetite, without the addition of silica. The lead fume produced by this operation (assaying 55-60 per cent. Pb) is collected in a baghouse used for this purpose only. The white metal and magnetite mixture, after being delead, are transferred from the lead-matte converter into a copper converter, in which a charge of copper matte has been poured, where it is slagged with silica and blown to blister copper. (For a detailed description of this procedure see paper¹ by O. M. Kuchs.)

Slags

The desired chemical analysis of a blast-furnace slag depends on several important factors; of prime importance in this state is the percentage of zinc on the charge. It is not our intention to go into detail in this matter of slag types and analyses, but merely to give an outline of general practice in the state.

The ores treated at Utah lead smelters have always furnished an excess of silica over iron and comparatively little lime; therefore, it has generally been necessary to purchase both iron and lime flux for making a desirable blast-furnace slag. As stated, iron flux is obtained in several different forms; lime rock, running over 50 per cent. CaO, is used for lime flux. Slags running from 5 to 13 per cent. ZnO have been regularly made at Utah smelters in comparatively recent practice. Typical slag analyses for these two extremes in ZnO content are as follows:

	PER CENT.	PER CENT.
SiO ₂	35.0	26.5-27.5
(Fe + MnO).....	32.5-33.5	40.0
CaO.....	20.0-21.0	11.0-12.0
MgO.....	1.0	1.5- 2.0
Al ₂ O ₃	2.5	2.5- 3.0
ZnO.....	5.0	13.0
S.....	1.0	1.5- 2.5

¹Lead-Matte Converting at Tooele. *Trans.* (1914) 49, 579.

Of course, there are many gradations between these two cases; it is necessary to lower both the silica and the lime content of a slag and raise the iron content as the zinc is increased and vice versa as the zinc is decreased. Where slags containing 10 per cent. or more of ZnO are run, trouble is usually experienced in furnace operation; these troubles do not arise from the presence of ZnO but from certain amounts of ZnS that often accompanies the oxidized zinc in the furnace charge. The ZnS fails, to a large extent, to enter either the slag or the matte but lies between the two in the form of a cold, mucky mass, which causes much trouble. Even with the greatest care in roasting, a considerable amount of ZnS may get into the furnaces. The use of special charges made up of good blast-furnace cleanings (largely slag) and a clean iron ore, which will smelt easily forming a slag high in iron and low in zinc, may be used to good advantage in alleviating the furnace troubles arising from zinc mush. Usually MgO and Al_2O_3 do not occur in sufficient amounts in the lead ores smelted in Utah to cause any serious trouble. Utah smelter slags are generally quite clean, as lead slags usually go, in lead, copper, and silver.

Lead Drossing and Casting

The lead is removed from the furnaces by the Arents' siphon tap, either by intermittent tapping or continuous overflow. A great deal of care must be taken to keep the lead well and connection to the crucible open and clean, especially where there is a high copper content in the charge. This is done by frequent rodding and scraping from the top of the lead well, followed at once by removal of the dross thus loosened and raised. If there is trouble in the bottom of the connection between the lead well and the crucible, which cannot well be gotten at from above, the introduction of compressed air (80 to 90 lb. pressure) through a long $\frac{1}{2}$ -in. iron pipe to the point of trouble has been found very beneficial. This air pipe is put into the crucible of the furnace through the tap hole. By constant care and the use of such remedies in the early stages of any trouble, Utah lead furnaces have been successfully operated on high copper charges for long periods without any serious crucible or lead-well trouble.

At all plants the lead is taken from the furnaces, to 30-ton drossing kettles, in small lead pots, drawn by hand. At two of the plants, a Howard Press is used for squeezing as much as possible of the molten lead from the dross; at the third plant, drain pans are used. At one plant, the lead is cleaned very thoroughly of copper (to 0.008 per cent. or less) by means of the Hulst decopperizing process, in which crude sulfur is stirred into the lead in the drossing kettle after the heavy dross has been skimmed off. At the other plants, copper removal from the furnace lead is accomplished entirely by cooling or cooling plus air agitation, thus

reducing the copper in the cast bullion to 0.05–0.08 per cent. The dross contains from 6 to 18 per cent. copper and 70 to 83 per cent. lead and runs quite high in silver and gold; it is all returned to the furnaces as a small part of each charge.

At two Utah plants, the bullion is siphoned from the kettles into molds of standard shape, where it is cast into pigs weighing about 90 lb. each. At the third plant, it is cast into anodes, weighing about 460 lb. each, for electrolytic refining. These pigs and anodes are weighed and loaded into railroad boxcars in which they are shipped to midwestern refineries. No lead refining is done in Utah.

Furnace Campaigns

The average length of campaigns of furnaces in Utah lead smelters is from 4 to 9 months; of course under unusual circumstances, a campaign may be shorter than 4 months. Generally these furnace campaigns are limited by stack accretions, which become so large at both ends of a furnace as to make operating conditions, especially on the charge floor, very unsatisfactory. Occasionally a furnace must be blown out because of crucible trouble.

Furnace Secondaries

All secondaries, other than flue dust and fume, such as cleanings from the tapping floor, settler cleanings, and furnace barrings, are either retreated in the blast furnaces direct or are sent to the D. & L. sintering machines. This latter procedure has the advantage that this class of material is usually an aid to good sinter making. The handling of flue dust and fume is described elsewhere.

Ventilation on Tapping Floor

At two plants, ventilation on the tapping floor is accomplished by positive fan suction applied at points of smoke production through pipes and hoods. These hoods, which may be raised and lowered by chains and counterweights, are placed over matte pot, tap hole and furnace spout, lead well, settler spouts, and slag pot. One fan, handling about 30,000 cu. ft. of air per minute will quite nicely take care of the smoke from five furnaces. All the fume and gas thus handled are delivered to a baghouse, where the fume is filtered out and saved. This fume will assay between 30 and 45 per cent. lead, 3 to 6 oz. silver, and 15 to 20 per cent. zinc. At the third plant, each furnace has an individual ventilation stack, about 45 ft. high with a cross-sectional area of about 80 sq. ft., which, in connection with a large hood, draws off the smoke from the tapping end of the furnace, matte pot, settlers, and slag pot. This system provides quite satisfactory ventilation, but does not permit of the saving of the fume.

Difficulties Encountered

The main difficulties encountered in lead smelting in this state arise from large amounts of zinc, copper, or arsenic on the blast-furnace charge. Zinc is generally the most prevalent of these three troublesome elements.

The main troubles, both metallurgical and economic, arising from a high zinc charge are: (1) Increased furnace delays and shorter campaigns as a result of stack accretions, (2) increased amount of secondaries to be retreated because of zinc mush in spouts and settlers, (3) increased slag losses because of the type of slag made necessary and to zinc mush, (4) increase in amount of costly iron flux required to produce the type of slag needed and a consequent reduction in the amount of ore charge smelted, and (5) general operating difficulties which are always encountered.

The main undesirable results of smelting a charge high in copper content (3 to 4 per cent. copper) are: (1) High percentage of coke necessary to obtain ordinarily good reduction, (2) slow furnace speed caused mainly by high coke charge used, (3) large matte fall required to care for the copper present, even when running matte up to 25 per cent. or more in copper content, (4) heat in upper part of furnace as the result of high coke charge, causing unusually large lead volatilization to baghouse, and (5) large amount of high copper dross formed in lead wells and in drossing kettles.

The presence of a considerable amount of arsenic on a blast-furnace charge, especially when coincident with a rather high zinc charge, which combination frequently occurs in this state, is productive of the following difficulties: (1) Formation of speiss in crucibles, (2) increase in percentage of coke needed and even then erratic reduction, (3) decrease in furnace speed, and (4) production of a high arsenic baghouse fume which has to be retreated with attendant difficulties.

Undoubtedly, other difficulties and economic losses in blast-furnace smelting may be directly attributable to the presence of large amounts of zinc, copper, and arsenic or a combination of two or more of them on the furnace charge, but those mentioned are sufficient to give an idea of why the lead metallurgist tries to avoid them when possible, and why they must be penalized when present in any considerable amount. Other elements, such as magnesium and cadmium, cause troubles when present in any considerable amount in combination with zinc, but these elements are not nearly as frequent trouble makers in this state as the first three mentioned. Cadmium at times is present in sufficient amount to cause trouble but magnesium rarely is.

Taken in all its various phases, the operation of lead blast furnaces on the charges that in recent years have been smelted in Utah is far from being simple metallurgy and requires much care and skill on the part of metallurgist and operators alike.

RECOVERY AND RETREATMENT OF FLUE DUST AND FUME

During the process of lead smelting, flue dusts and fumes are produced in such quantities that the recovery of these plant secondaries has become of sufficient importance to the smelter to warrant the installation of expensive apparatus. There are four sources from which dusts and fumes are obtained: roasters (Wedge, Godfrey, McDougall), Dwight-Lloyd sinter machines, converters, blast furnaces.

The terms "flue dust" and "fume," as applied to smelter products, may be defined in the following manner to establish the differentiation that actually exists between the two: *Flue dust* is that part of the fines in the feed or charge that is carried into the flue system from the furnace by suction or draft; *fume* is a product of distillation or sublimation, due to the heat of chemical reaction and heat combustion within the furnace, subsequently condensed by cooling. This product is drawn into the flue system by suction or draft.

The three lead smelters in Utah have adequate equipment for recovering the flue dust and fume produced, though methods differ considerably in the general means employed. There are three primary methods in use: (1) Mechanical precipitation (where flue dust content is high), (2) filtration baghouses (for fumes not acid), (3) electrical precipitation units, Cottrell treaters (for flue dust and fume).

Roaster Flue Dust and Fume

In the preroasting of ores for sulfur elimination by calcination in McDougall, Godfrey, or Wedge roasters, the gases carry considerable flue dust, with small amounts of fume, and the dust caught in the flues exists physically in a more or less minute, granular form with an analysis quite similar to that of the feed mix. The practice at the various smelters is to catch mechanically as much of the heavier dust as possible in flues leading from roasters, with baghouses and Cottrell treaters farther along the flue system for additional precipitation of dust and fume. Roaster flue dust differs from roaster fume; physically with respect to fineness, also chemically to a marked degree.

At one smelter, the method of flue dust and fume recovery from McDougall roaster gases is as follows: Two large brick flues, hopper bottomed, conduct the gases directly to a rectangular brick dust chamber 120 ft. wide, 140 ft. long, and 60 ft. high. The dust chamber is hopper bottomed with three tunnels beneath, for dust removal. A very slow gas velocity is maintained in the flue and chamber to permit the dust to settle out. From the chamber the gases enter a two-unit electrical precipitator. This Cottrell treater is of the horizontal flue type, with the two units in parallel. It is equipped with corrugated sheet-iron plates, suspended vertically, as collecting electrodes; and with $\frac{1}{4}$ -in., standard,

wrought-iron pipes as discharge electrodes. Each unit of the treater consists of two separate sections in series, one with the other. Dependent on the number of roasters in operation, a gas volume of 8000 to 16,000 cu. ft. per min. is treated with a velocity of 9 to 18 ft. per sec. at a temperature of about 220° F. Sufficient temperature is held to prevent corrosion due to acidity. The treater hoppers deliver the dust to screw conveyors, which in turn deliver to a large steel storage hopper at the back end of one of the tunnels under the dust chamber. The dust is drawn from this storage hopper into small covered cars for interplant transfer. The treater walls, and as much as possible of the roof, are built of Johns-Manville transite (asbestos board) which has proved very satisfactory, no transite having been replaced during the life of the treater, about 7 years. The dust is shaken from the electrodes by hand-operated knockers. No conditioning of the gases is necessary. Natural draft is furnished by a 350-ft. brick stack, connected to the Cottrell treater by a large brick flue.

The dust drawn from the flues, dust chamber, and treater is taken direct either to the copper plant or lead plant (Dwight-Lloyd sintering machines) according to its lead content. The efficiency of this treater has been exceptionally high, throughout its period of operation.

At another smelter where preroasting is obtained by calcination in Wedge and Godfrey roasters, the general practice of handling the gases is as follows: The Godfrey roasters deliver their gases to a large brick flue, which in turn delivers to a large brick main flue that acts as a common carrier for these, as well as the gases from the Wedge roasters and Dwight-Lloyds, delivering the combined gases to a Cottrell treater system. The velocity of the gases from the Godfreys is unusually high, with consequent little accumulation of flue dust. The Wedge roaster gases enter a brick dust chamber, 36 ft. wide, 36 ft. high, and 250 ft. long, by individual, small-flue connections. The chamber is hopper bottomed with a tunnel underneath for dust removal; from here the gases pass to a large brick flue which, in turn, delivers to the larger brick main flue and to the Cottrell treater system. The dust drawn from the Godfrey flue is transferred, in small cars, to the Dwight-Lloyd feed bins direct. This dust has practically the same analysis as the Godfrey feed.

The Wedge roaster flue dust is drawn from the chamber and flue into small push cars, which are used to transfer the dust direct to large cars receiving the calcine from the wedges; the mixture goes to the Dwight-Lloyd plant.

The combined gases from the Godfrey and Wedge roasters, together with the Dwight-Lloyd gases, are delivered to a three unit Cottrell treater, which is built of brick. These three electrical units are so arranged as to divide the gas stream, half going to each of two units, A and B, in parallel; and then, combining again, passing on to Unit C.

By damper control, the gases can be treated in series only, if desired. Conditioning of the gases with H_2SO_4 fumes is necessary at times. These fumes are introduced into the main flue, about 100 ft. in front of the treater, by means of small furnaces.

The treater is of the pipe type, equipped with 6-in. pipes, 12 ft. long, as the collecting electrodes, and steel wires as the discharge electrodes. The average volume of gas treated is about 250,000 cu. ft. per min. with a velocity of 6 to 15 ft. per sec. Updraft is used on all three units. Units A and B have six sections each; and unit C eight sections, with 200 pipes to a section. The dust is shaken from the electrodes by mechanical devices. Forced draft is obtained by means of a large fan at treater outlet, which delivers to a 450-ft. brick stack.

The treater is flat bottomed and the dust is cleaned out by hand into small cars, delivering the product to a pugger where it is converted, by the addition of water, to a "mud." This "mud" is transferred to the blast-furnace plant and put on the charge direct.

At the other smelter, Wedge roasters used for preroasting sulfide ores deliver their gases to a baghouse by means of a system of three large cylindrical steel flues. These cylindrical steel flues, hopper bottomed, are in parallel and are connected to one another by an intricate system of "A" pipes so arranged as to cool the gases sufficiently by radiation before delivery to the baghouse. The gases from the Dwight-Lloyds join the roaster gases before their entry to the baghouse.

This baghouse is a brick building 283 ft. long, 56 ft. wide, and about 55 ft. high, containing 3340 woolen bags $33\frac{1}{2}$ ft. long and 18 in. in diameter. It has eight equal sections, or bays, equipped with hoppers in which screw conveyors operate to remove the fume and dust. The method of shaking the bags is by reverse current assisted by hand shaking. Only six of the eight bays are used to filter these roaster and sinter plant gases, the remaining two being used for blast-furnace gases. The filtered gases are delivered to a brick stack 450 ft. high, furnishing the necessary baghouse draft.

The dust drawn from the cylindrical steel flues, as well as the baghouse fume from roaster sections, is transferred in small cars to the brick press for briquetting into $7\frac{1}{2}$ -lb. bricks, which are used directly on the blast-furnace charge.

Dwight-Lloyd Flue Dust and Fume

In further eliminating excess sulfur from ores, by means of sintering on Dwight-Lloyds, the gases carry considerable fume with only a small amount of flue dust. These products often contain sufficient elemental sulfur to render them combustible or explosive. Because of its extreme fineness, the recovered product is very light and fluffy. To obtain effi-

cient recovery, mechanical precipitation cannot be depended on, but baghouses or Cottrell treaters are employed.

At one of the smelters the Dwight-Lloyd gases are drawn off through the wind boxes of each machine by individual fans delivering through a small brick flue into a larger transite flue. From here, the gases pass to a Cottrell treater system connected by a large transite and steel flue to a 200-ft. brick stack. This stack also receives the filtered gases from the blast-furnace baghouse.

The Cottrell treater is a four-unit, pipe-type precipitator, equipped with pipes 15 ft. long and 12 in. in diameter as collecting electrodes; and iron wires as discharge electrodes. Each unit has two sections, with 110 pipes to a section. By damper control, the treater can be operated by either downdraft or updraft, with all four units in parallel; or it can be operated with the first two units in series with the second two. With four sinter machines, the gas volume is about 100,000 cu. ft. per min.; and with six machines, about 150,000 cu. ft. per min. The dust and fume are shaken from the electrodes by electrically operated knockers. Forced draft is obtained by the use of a large fan in treater outlet flue near the stack. The Johns-Manville transite (asbestos boards) in use on the treater and flues has proved satisfactory. The treater is hopper-bottomed with screw conveyors to remove the dust.

The dust drawn from the flues and treater goes direct to the Dwight-Lloyd feed mixer when not high in arsenic or, if the arsenic content is high, is transferred in cars to the arsenic-plant feed bins.

At another of the smelters, the Dwight-Lloyd gases are drawn off through the wind boxes by individual fans to a large brick flue, which in turn delivers to a larger brick main flue, which acts as a common carrier for the gases from the Wedge and Godfrey roasters. This main flue delivers the combined gases to the three-unit Cottrell treater system, as described under Roaster Gases. Because of the high velocity in the flues, the settling of dust is small. Whatever dust is removed from the flue is returned direct to the Dwight-Lloyd feed.

At the third smelter, the Dwight-Lloyd gases are drawn through the wind boxes by individual fans and delivered to a steel flue with a concrete base, which conveys the gases to a series of twelve cooling flues. These join the flue carrying the Wedge-furnace gases, which is connected to the baghouse. The dust from the steel cooling flues and roaster section of the baghouse (six bays) is briquetted and used directly on the blast-furnace charge.

Blast-furnace Dust and Fume

The method of recovery used on blast-furnace gases throughout the state is virtually the same, excepting for slight modifications in the flue system; baghouses are employed to filter these gases. At one smelter,

the furnace gases pass through steel downtakes into cylindrical, steel dust catchers, 20 ft. in diameter and 18 ft. high. The gases enter the dust catchers near the bottom on a tangent and pass out through a conical top to the main flue. The dust collected in these catchers discharges through openings in the bottom on to a 16-in. belt conveyor, which delivers it to railway cars. The main flue is of the balloon type, made of "Keystone" steel, with a continuous hopper bottom. This flue, which is 498 ft. long, delivers the gases into a baghouse. This building is of brick, 154 ft. long, 55 ft. wide, and 50 ft. high, and is divided into ten sections, or pits. Each section contains 144 woolen bags 30 ft. long and 18 in. in diameter. The pits are flat bottomed and the fume is removed by hand after burning. Bag shaking is accomplished by reverse current. This fume averages about 45 per cent. lead and 15 per cent. arsenic. When five blast furnaces are in operation, the gas volume is about 90,000 cu. ft. per min. These gases are drawn from the furnaces and forced through the baghouse under pressure by means of a large fan. From the baghouse, the gases pass through a steel downtake by suction, which is furnished by the 200-ft. brick stack, which is also connected to the Dwight-Lloyd system.

The dust and fume from the dust catchers and main flue are drawn off into cars and delivered to the Dwight-Lloyd feed bins direct. The burned baghouse fume, when low in arsenic, is returned direct to blast-furnace bins. When the arsenic content is high, the fume is crushed and delivered to the arsenic plant, where it is mixed in with the general feed in quantities equal to production.

At another smelter, the blast-furnace gases are drawn off through brick downtakes to a large hopper bottomed brick flue, acting as a dust catcher, then through 1270 ft. of rectangular, flat-bottomed, brick flue and discharged, by means of a Buffalo exhaust fan, into a baghouse. This baghouse, a brick structure 216 ft. long, 90 ft. wide, and 60 ft. high, contains four compartments, each compartment containing 1008 woolen bags. The bags are 30 ft. long and 18 in. in diameter. Bag shaking is accomplished by hand. The maximum gas volume capable of filtration in the baghouse is 500,000 cu. ft. per min.; and when five furnaces are operating about 120,000 to 130,000 cu. ft. per min. is filtered. Only three-quarters of this baghouse is used to filter blast-furnace gases; the remaining quarter is used to filter arsenic-plant gases. The dust from the connecting flues to the baghouse, together with the burned baghouse fume, is shipped to the company's refinery in another state, or is treated in the plant arsenic furnaces. The fume averages about 50 per cent. arsenic and 15 per cent. lead.

At the third smelter, the blast-furnace gases pass to two baghouses, one at each end of the system. One quarter of the north, or brick, baghouse is devoted to blast-furnace gases. This house contains 832 woolen

bags, $33\frac{1}{2}$ ft. long and 18 in. in diameter. At the south end, the furnace gases pass through a 16-ft. steel, balloon flue, coated with gunite; this flue is about 100 ft. long. At its south end, this flue connects with a baghouse built of corrugated iron lined with transite. This baghouse is 139 ft. long, 47 ft. wide, and 23 ft. high and has five bays containing 1200 woolen bags of the same length as in the brick baghouse, but only 12 in. in diameter. The fume is dropped into hoppers, from which it is drawn into small tram cars for transfer to the arsenic plant. The fume contains 45 to 60 per cent. arsenic and 12 per cent. lead. The flue dust from the chamber is transferred to the brick press, where $7\frac{1}{2}$ -lb. bricks are made; these are returned to the blast-furnace charge.

Converter Fume

The practice of blowing hot lead-copper matte in converters is carried out at but one of the lead smelters. The object is to drive off the lead as an oxide, lead oxide, and basic lead sulfate (PbO and NPbO.PbSO_4) and recover the copper as bullion.

The gases from the lead converters are drawn through a long steel flue equipped with a continuous hopper bottom, and forced into a baghouse under pressure by means of a fan. The baghouse delivers the filtered gases to a brick stack 150 ft. high.

The baghouse is a brick structure 122 ft. long, 44 ft. wide, and 50 ft. high. There are eight compartments, each containing 120 woolen bags, 30 ft. long and 18 in. in diameter. Each compartment is hopper bottomed with a screw conveyor, for the delivery of the fume to a main screw conveyor, which in turn delivers to a pugger for moistening before delivery to a railway car. The fume is slaken from the bags by means of a reverse air-current system. This baghouse was designed for a gas volume of about 150,000 cu. ft. per min.

The pugged fume, when sufficiently high in arsenic content, is sent directly to the arsenic-plant bins; when low in arsenic content, it is delivered to the blast-furnace charge bins. The average analysis of this fume is about 55 per cent. lead and 15 per cent. arsenic.

Arsenic Fume

The recovery of arsenic from fume and flue dust is practiced by the three lead smelters, each plant modifying the general scheme to suit its own requirements. The general scheme is to sublime or distill off the As_2O_3 fume by roasting, and then, by cooling, cause the fume to condense out in kitchens or chambers where it can be recovered.

At one of the smelters, McDougall roasters are used to roast off the As_2O_3 fume, which is delivered to other McDougall roasters, connected in series, acting as condensing chambers. Two roasting furnaces are connected to two other furnaces, acting as first condensing chambers.

These two first condensers are connected to a fifth furnace, acting as a common second condensing chamber. The second chamber is connected to a baghouse. The fume is drawn through the roasters by a fan and forced through the baghouse under pressure. This baghouse contains 48 woolen bags 17 ft. long and 18 in. in diameter, and is hopper bottomed. The baghouse was designed to handle 3000 cu. ft. of gas per minute. The fume is shaken from the bags by hand shakers.

The fume caught in the condensing chambers averages about 94 per cent. As_2O_3 and is refined at another plant of the company. The fume caught in the baghouse is low in arsenic content and is returned direct to the arsenic plant feed bins for retreatment. The residue, or calcine, from the roasting furnaces is delivered to the blast-furnace charge bins, or is shipped to the cadmium plant at another Utah smelter, if it contains sufficient cadmium.

The As_2O_3 fume in the condensing chambers is removed by running these roasters at regular intervals, the fume being raked down into the furnace hoppers. These hoppers deliver the fume to a drag-chain conveyor leading to a mechanical barrel-packer for shipment.

At another smelter arsenical material is treated in Godfrey roasters; two roasters being used for this purpose. The fume is drawn off by fan suction through a set of arsenic kitchens, acting as condensing chambers, and forced through one quarter of the blast-furnace baghouse under pressure. This section of the baghouse contains 1008 woolen bags 30 ft. long and 18 in. in diameter, with a maximum filtering capacity of 75,000 cu. ft. per min. The arsenic kitchens are divided into four groups, each group containing four sections, giving a total of sixteen passages for condensation. The As_2O_3 fume recovered runs about 93 per cent. As_2O_3 and is shipped out as crude As_2O_3 to this company's refinery in another state. The residue, or calcine, from the Godfreys is returned to the blast-furnace charge.

At the other smelter, the arsenical material is roasted in three Brunton furnaces. The fume is drawn off by fan suction through a set of arsenic kitchens consisting of 12 compartments, which act as condensing chambers, and is forced through a baghouse containing two sections, each having 108 bags 25 ft. long and 12 in. in diameter. Usually one section is in operation at a given time, and is capable of filtering about 2000 cu. ft. of gas per min. The residue from the Brunton furnace goes to a brick press, thence to the blast-furnace charge, or transferred to the cadmium plant if cadmium is high.

The crude fume recovered from the kitchens contains about 93 per cent. As_2O_3 and is again roasted in two reverberatory type furnaces. The fume from these furnaces is drawn off through another set of arsenic kitchens, consisting of twelve compartments, acting as condensing chambers, and is forced through a baghouse containing two sections, each

having 30 bags 25 ft. long and 12 in. in diameter. Only one section is in operation at any given time and is capable of filtering about 1000 cu. ft. per min. The refined As_2O_3 fume recovered from the kitchens containing 99 per cent. As_2O_3 is barreled and marketed.

Cadmium Recovery

The recovery of cadmium is practiced at but one smelter, where the electrolytic process is used. The cadmium-bearing material is mixed with H_2SO_4 and roasted in a reverberatory furnace to convert to sulfates. After roasting, it is delivered to a ball-mill for grinding, then agitated in a Pachuca tank with water to bring about the solution of water-soluble sulfates. From the Pachuca tank, the contents go to a filter press; the filter cake then goes to the brick press for blast-furnace charge and the solution goes to the electrolytic cadmium tanks. Sheet cadmium is deposited on aluminum cathodes. The metallic cadmium is stripped from the cathodes, melted, cast into sticks weighing about 5 oz. and marketed.

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DISCUSSION

D. W. JESSUP, Midvale, Utah.—At Midvale, the first matte contains from 10 to 12 per cent. copper; at Tooele, the first matte carries 20 per cent. copper and is blown in a converter to 50 per cent. copper. Would it be practical for other smelters, producing 100 tons of low-grade matte per day, to install a converter and blow the matte instead of making a copper-concentrating run in the blast furnace? If this were feasible, there would be a saving of metals, especially lead; the converter slag would be returned to the Dwight-Lloyd machines, producing a better sinter; the iron in the matte would be of value, saving the cost of iron flux; the coal would probably be less.

B. L. SACKETT.—When conditions are unusual, as at Tooele, where a copper and a lead smelter are under one roof, so to speak, we necessarily have our own converting plant for the handling of copper matte. We, therefore, adopted the simplest and most effective way of handling the lead-blast furnace matte; that is, by taking it hot from the blast furnaces and utilizing that heat in the converters, therein eliminating the lead as fume, which is recovered and retreated. The copper remains as a

residual material in the lead converter, which is transferred to a converter containing copper matte from the reverberatory furnace and blown to blister copper. Whether or not the installation of a converting plant at a lead smeltery, where no copper work was being done, would be worth while would depend entirely on conditions at that plant and the economic outcome to be figured in favor of or against such an installation.

E. H. LAWS, Carnegie, Pa.—The paper states that all the dross is returned to the furnaces as a small part of each charge. At Salida, in smelting 500 tons of charge per day to produce 45 tons of bullion, the dross production varied from about 5 tons, on ore smelting, to 15 tons, when matte was being concentrated; this was all returned to the charge. Although this dross formed a small part of each charge, the percentage of lead and copper returned was considerable, and subsequent experience has convinced the writer that the smelting of this dross with high-grade galena in a reverberatory furnace, should have been considered, even on this comparatively small tonnage. The practice at lead refineries where undrossed bullion is tested is along this line, and it has been tried at some smelting plants. Lead, matte, and slag are produced. The matte is returned to the charge in place of galena until it contains 50 per cent. or more of copper and only the leady slag, containing some of the copper, goes to the blast furnace.

At Northport, with a high-lead charge and heavy production of matte, the formation of dross was excessive, part being lead sub-sulfide. This caused great difficulty in furnace operation and increased refinery expense, as the bullion was shipped without drossing. The dross production decreased as roasting practice improved. When the matte fall was reduced practically to zero by double roasting, it was found that under conditions of a heavy lead fall, a very small matte fall and strong reduction, only clean lead with a small amount of matte was produced, the matte forming a thin skim at the top of the lead bar as cast at the lead-well. When afterwards we began to return dross to the blast-furnace charge, we hoped to produce a small percentage of matte rather high grade in copper and little dross. We were able to control the percentage of matte fall but were not able to raise the grade of the matte, and a large part of the copper went into dross and into slag. Dross is practically all metal and it is reasonable to expect that furnace operation will improve and metal recovery increase if the dross can be kept away from the blast-furnace charge altogether.

Another point worth consideration is the handling of Cottrell process fume. The Northport plant handled successfully, a mixture of sintering-machine and blast-furnace gases, which were conditioned by water sprays. Because much trouble was experienced from spontaneous ignition of the fume, the steel collecting hoppers were replaced with brick cellars. The fume burned readily to a grayish material, the fines being granular

and the lumps of a cokelike structure. This burned fume could be handled much more easily and safely than the unburned fume, and was shoveled into railway cars, which ran between the two rows of cellars. At first, we attempted to smelt this burned fume direct on the blast furnaces; this resulted in the formation of crusts in the tuyere zone, which caused serious trouble. The fume was then single-roasted and then double-roasted, as a part of the regular sintering machine charge, and no difficulty was experienced in its use.

B. L. SACKETT.—At the Tooele plant, we treat a charge at our lead-blast furnaces that is comparatively high in copper content and have a correspondingly high dross fall. The dross produced will amount to approximately 18 to 20 per cent. of the furnace lead. This dross is pressed and returned to the blast furnaces, where it is added at the rate of a few hundred pounds to each charge. There are times when, due to some unusual labor condition, we are not able to put the dross back to the furnaces for a period of several shifts; this necessitates later putting on larger amounts of dross to catch up. We have not noticed any particular difference in furnace operation or speed during the periods when the dross is entirely off or is put on in unusually large amounts. At the Tooele plant, returning the dross to the blast furnaces has made very little if any difference in the lead content of the slag produced or in the tonnage of other charge handled by the furnaces.

The Chief Consolidated Volatilization Process and Mill

By G. H. WIGTON,* EUREKA, UTAH

(Salt Lake City Meeting, September, 1925)

THE oxidized ores of the Chief Consolidated Mining Co., in the Tintic mining district, have never yielded to metallurgical treatment by any standard method except smelting. These ores occur in comparatively small, irregular, siliceous replacements in limestone, and carry silver, lead, and gold as the principal valuable metals. But smelting methods are unsatisfactory, as the lead smelters heavily penalize the large amount of silica in the ore, and the copper smelters do not pay for the lead in the ore; therefore, an alternative treatment method was sought.

In 1916, a metallurgical research department was organized under the direction of the writer. Many standard metallurgical methods were investigated but, on oxidized ore, none yielded extraction great enough to make its use feasible. During some chloridizing-roasting experiments in 1916, made in an assay muffle, the writer noted that large proportions of the silver, lead, and gold were volatilized from certain oxidized ores. The possibility of volatilizing the metals and collecting them in the form of a concentrated fume was then studied. But, as it was shown that satisfactory chloride-volatilization would be limited to a furnace feed with a high fusing temperature of the non-volatilizable constituents, and as the results obtained in a rotary kiln with the admixture of common salt with the ground ore were inferior to muffle tests, further volatilization experiments were discontinued until 1920. During this interval, an experimental sulfidizing and flotation plant was operated.

After the cessation of attempts to float the oxidized minerals, chloride-volatilization experiments were resumed. The highly infusible flotation tailing from the operation of the flotation mill was used for furnace feed. The first tests made on flotation tailing mixed with 10 per cent. common salt showed nearly complete lead and gold volatilization but considerably less volatilization of silver than in muffle tests. In attempts to increase the silver extraction, the percentage salt in the furnace feed was varied, and it soon became apparent that the use of smaller percentages of salt raised the fusion temperature of the furnace charge and thus

* Metallurgical Engineer, Chief Consolidated Mining Co.

permitted the use of higher temperatures, which in turn resulted in increased silver extraction. Finally, the addition of salt or other chlorides to the furnace feed was discontinued and, with the increased temperatures permissible, nearly complete volatilization of the gold, silver, and lead was obtained in the experimental rotary kiln.

The elimination of salt from the furnace feed has made volatilization much more desirable because: (1) It greatly increases extraction. (2) It results in the production of a fume substantially free from chlorides, and which therefore requires no intermediate chemical treatment before blast-furnace reduction. (3) It produces a furnace gas free from chlorine or hydrochloric acid, and one that can be readily filtered in a baghouse with nearly complete recovery of fume. (4) It eliminates the cost of the salt itself. These marked improvements over chloride volatilization



FIG. 1.—GENERAL VIEW OF CHIEF CONSOLIDATED CONCENTRATOR, EXPERIMENTAL PLANT IN DISTANCE.

resulted in the decision to build a complete test plant in which quantitative results could be obtained in a continuously operating process.

Ores from the Chief Consolidated mines vary from entirely oxidized ores to ores showing only slight oxidation, and from nearly self-fluxing ores to highly infusible ores. As has been stated, a furnace feed with a high fusion temperature of the non-volatilizable constituents is necessary for complete volatilization of the valuable metals; therefore, to increase the proportion of ores available for milling, it is desirable to remove, by concentration, some of the constituents that tend to promote fusion of the furnace feed or to hinder volatilization. As gravity concentration and flotation methods can readily remove as concentrate nearly all the sulfide minerals, as well as considerable lead carbonate, with the production of a highly siliceous residue containing the remaining oxidized metals, a test plant was erected in which these methods preceded volatilization. The advantages of this preliminary concentration on Chief Consolidated ore are as follows:

Lead sulfide and silver-bearing iron sulfides as well as some lead carbonate are removed as marketable concentrate.

The removal of iron, sulfur, and lead from the furnace feed raises the fusion temperature of the residue, and thus permits greater extraction of the valuable metals by volatilization.

The removal of sulfides from the furnace feed insures the production of a basic, non-corrosive furnace gas that can readily be filtered through cotton or woolen bags.

The removal of sulfur from the furnace feed eliminates the necessity of any preroasting.

The removal of concentrate decreases the tonnage of feed to be handled by the furnace.

Preliminary concentration permits the treatment of ores that could not otherwise be treated by volatilization.

The concentration methods, when employed on the small proportion of ores free from oxidation, afford a recovery great enough to eliminate the necessity for subsequent treatment by volatilization, and therefore constitute a complete treatment for this class of ore.

EXPERIMENTAL PLANT

The experimental plant consisted of a gravity concentration and flotation unit and a volatilization unit, and was designed to treat continuously about 5 tons of ore daily with equipment that duplicated, except in size, that which would be used in a commercial plant. The flow sheet and equipment of the experimental plant are as shown in Fig. 2.

Continuous operation of the wet-concentration plant presented no unusual difficulties, but troublesome accretions formed in the rotary kiln and had to be removed each shift with a hand bar. Extractions in this rotary kiln were excellent, provided a long flame was used. The baghouse recovered all visible fume; and as the fume was highly basic, no bag trouble developed.

The troublesome furnace accretions seemed to occur in the preheating zone of the kiln, up to a temperature of about 2000° F., but at higher temperatures they did not exist. They were not slagged accretions, such as the rings in cement kilns, but consisted of unfused particles of quartz, the principal gangue, loosely bound together by slight fusion of other gangue constituents. They did not occur as definite rings, as in cement kilns, but occupied the entire preheating zone. On account of the comparatively unfused condition of these accretions, it was thought that their own weight would make them drop from the lining of a larger kiln on account of the greatly flattened arch.

To determine whether a commercial-size kiln would make the same extraction as the experimental kiln, and whether the accretions in a large kiln would be serious, 1000 tons of oxidized tailing were sent to the

plant of the Ogden Portland Cement Co. for test in its $7\frac{1}{2}$ by 125 ft. rotary kiln. Here it was definitely determined that good extractions could be made in the large kiln, but that the soft accretions grew just as fast as in the small kiln. Moreover, it was impossible to remove accretions from the large furnace by the usual methods, so that after 48 hr. operation the opening in the kiln was closed so much by this peculiar growth that it was impossible to continue operations. In other words, the commercial-size kiln acted exactly the same as the experimental kiln but, on account of its increased size, it was impossible to remove the accretions by hand poking. Until a mechanical arrangement capable of

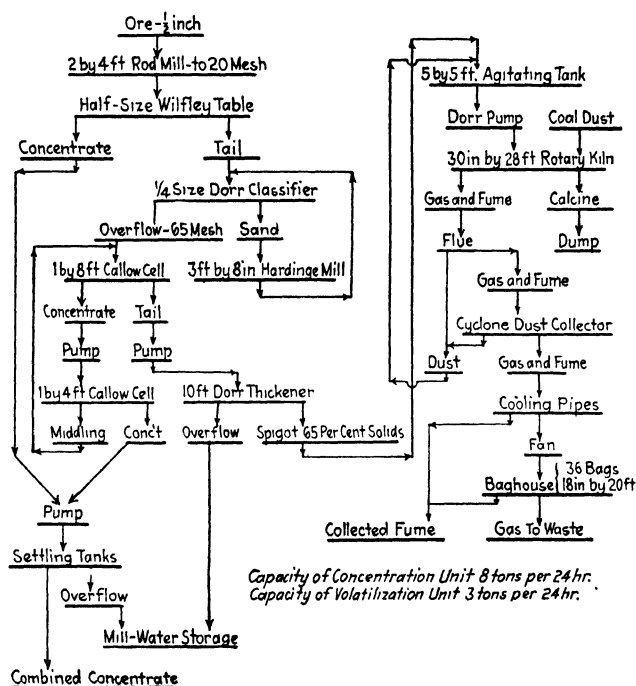


FIG. 2.—FLOW SHEET OF EXPERIMENTAL PLANT.

removing these accretions and adaptable to commercial-size kilns was devised, or until a method of controlling the accretions was found, it was not considered feasible to proceed with the erection of a commercial plant.

The next work in the experimental plant was to find a practical method of controlling the kiln accretions, and one that could be applied to a full-size rotary kiln. Finally, a water-cooled reciprocating rabble that worked continuously in the kiln from the feed, or flue, end was devised. This kept the experimental kiln free from accretions, but it was occasionally necessary to run the rabble into the hot zone. With this

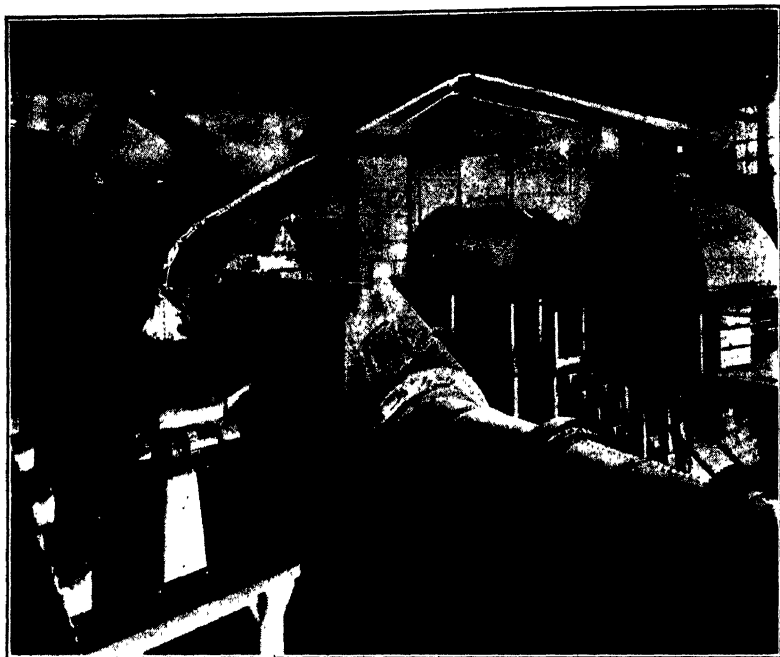


FIG. 3.—KILN BUILDING, SHOWING RUGGLES-COLES DRYER AND PORTLAND FILTERS.

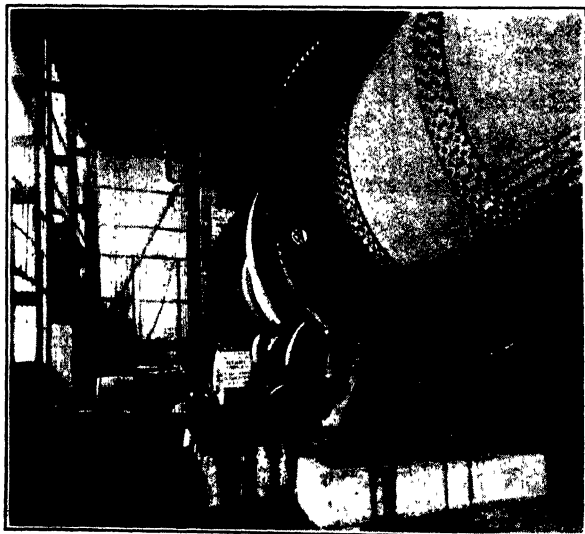


FIG. 4.—DRIVE OF 10 BY 80 FT. KILN.

equipment, the experimental kiln was run nearly continuously from June 6 to July 21, 1923, with the following results:

EXPERIMENTAL PLANT RESULTS

	Au, Oz.	Ag, Oz.	Pb, PER CENT.	Zn, PER CENT.	Fe, PER CENT.	Ins., PER CENT.	S, PER CENT.	CaO PER CENT.
Ore.....	0.055	25.2	6.0	4.6	7.0	63.8	4.8	2.6
Concentrate.....	0.23	172.6	39.8	7.9	11.3	11.6	15.2	1.0
Furnace feed.....	0.044	15.9	3.9					
Fume.....	0.18	60.5	14.0	4.0	5.3	46.4	1.8	4.0
Calcine.....	0.005	1.6	0.12	0.0	5.0	89.2	0.1	1.4

Fire, pulverized coal.

Furnace feed, 80 mesh

Average hot-zone temperature, 2550° F.

Average flue temperature, 1000° F.

Average recovery of fume in baghouse, by test, 99.74 per cent.

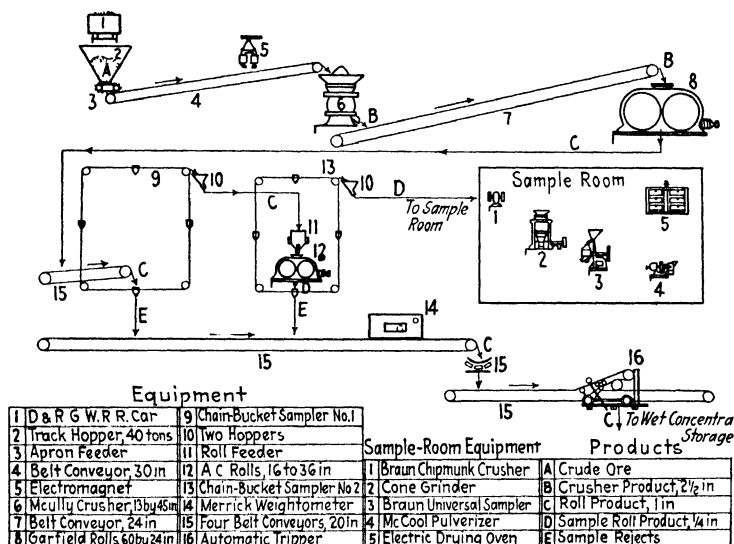


FIG. 5.—FLOW SHEET CHIEF CONSOLIDATED CRUSHING PLANT; NORMAL CAPACITY 65 TONS PER HOUR.

Although this test showed high metal recoveries, the process was still open to the objections that operation of the kiln in this manner produced a large amount of flue dust that required retreatment and lowered the grade of the fume, and that the continuous operation of the water-cooled rabble in the furnace increased the fuel consumption. Also, the maintenance cost of the rabble was excessive. To obviate these objections, the tailing from the wet-concentration mill was filtered, dried, and fed into the firing end of a rotary kiln 3 ft. in diameter by 18 ft. long. In this manner, the feed was quickly heated above the temperature of accretion

formation, so that the accretions occurred only in the first few feet of the kiln and could, therefore, be much more readily removed by intermittent poking, either by hand or mechanically. This quick heating also resulted in quick softening of the furnace feed, the prevention of nearly all dusting, and the production of a fume containing only about 15 per cent. silica. Extractions were about the same as when the kiln was fired at the discharge end. This concurrent furnace had a capacity of about 6 tons per 24 hr., with a pulverized-coal consumption of 33 per cent. of the furnace feed. After these satisfactory results had been obtained, the decision to build a commercial plant was reached.

THE CHIEF CONSOLIDATED MILL

The site selected for the Chief Consolidated mill is about 2000 ft. east of the Chief Consolidated mine at Eureka. It overlooks a long

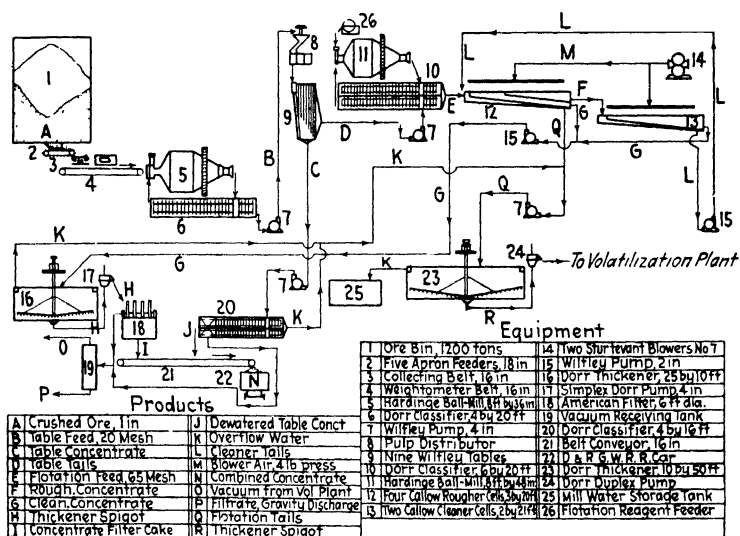


FIG. 6.—FLOW SHEET OF WET CONCENTRATOR; NORMAL CAPACITY 300 TONS DAILY.

slope above the town that will afford ample room for stacking the dry tailing.

In the design of the mill, the flow sheet developed in the experimental plant was closely followed. The concentration and volatilization units were designed for an ultimate capacity of 250 tons of ore per 24 hr., but the crushing plant and coal-pulverizing plant were designed to handle the necessary tonnage in an 8-hr. shift. The accompanying flow sheets (Figs. 5 to 8) will show the principal equipment in each department. The plant is substantially constructed of concrete and steel. Wherever practicable, positive, individual drives were used on all machinery. The electrical equipment of the plant is especially efficient, with push-button

or automatic control for all motors, and with adjustable speed motors on all feeding devices.

The crushing plant includes equipment for sampling and weighing each carload of ore for settlement with the mining department. A unique feature of this plant are the samplers, which consist of a number of pivoted buckets that not only sample the ore, but also elevate and convey it to the regrinder.

The wet concentration plant is so designed that it can be intermittently operated either on sulfide ore, with the production of a concentrate and finished tailing, or on oxide ore, with the production of concentrate and a product that goes to the volatilization plant for final treatment.

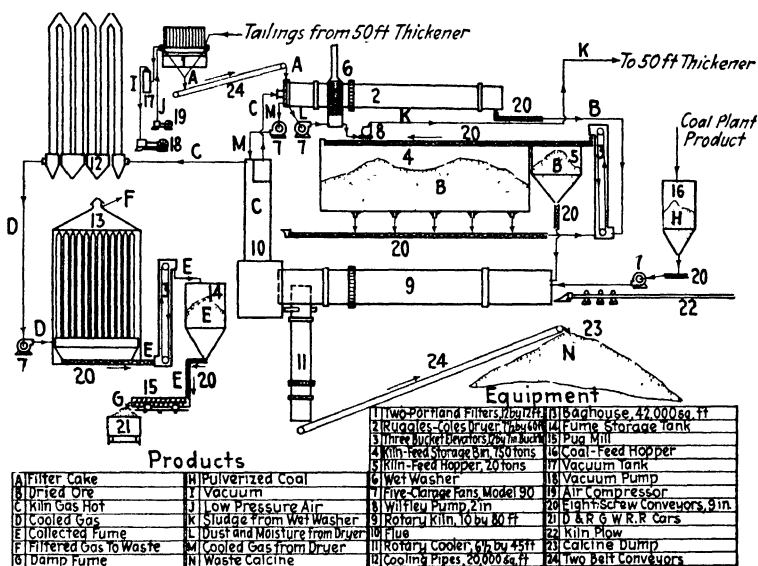


FIG. 7.—FLOW SHEET OF VOLATILIZATION PLANT.

It is also possible to eliminate the regrinding of oxide ore in order to deliver a 20-mesh feed to the volatilization plant. No attempt is made to recover any of the oxidized minerals by flotation, as that is the function of the volatilization plant.

The volatilization plant includes not only the rotary kiln for volatilization, but also equipment for filtering and drying the furnace feed. Heat for the drying operation is supplied entirely by the hot flue gases from the rotary kiln. In order to prevent contamination of the fume-bearing flue gas, it was necessary to make the drying a muffle operation; therefore the rotary dryer is of the indirect-heat type. Drives on the rotary kiln, coal-firing equipment, and fans furnishing the furnace draft are equipped with adjustable speed motors to furnish extreme flexibility in operating conditions. The rotary-kiln drive includes supplementary storage

batteries sufficient to drive the direct-current motor for a short period in case of power interruptions; this provision was made to prevent the hot charge from sticking to the kiln lining. The water-cooled plow for removing kiln accretions was built after the rest of the plant had been placed in operation; it consists of a plow mounted on the end of a water-cooled bar, 86 ft. long, with a direct-current crane motor and gears mounted on the other end. The gears run on stationary steel rack mounted on each side of the bar.

The baghouse is similar to those used in most lead smelters. The illumination equipment for detecting bag leaks and the automatic shaking system are features in this plant.

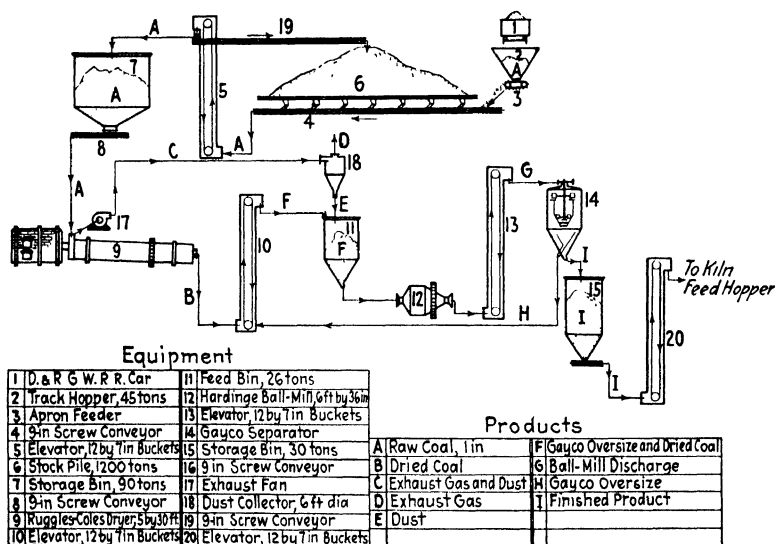


FIG. 8.—FLOW SHEET OF COAL-PULVERIZING PLANT.

The coal-pulverizing plant is unique among western plants, in that it employs a ball-mill working in closed circuit with an air-separator for the pulverizing.

In August, 1924, the wet concentration plant started operations on sulfide ore. This department developed no serious trouble and yielded expected metallurgical results. The volatilization department was ready to start operations in December, 1924, but as considerable trouble developed in the operation of the rotary kiln, it was not operated steadily until May, 1925. The most important development in this plant was the successful operation of the mechanical water-cooled plow for removing furnace accretions. With this plow, a series of longitudinal trenches can be cut through the accretions whenever necessary, and a clean furnace can thereby be maintained. The actual plowing operation requires about 20 minutes.

As the final plant adjustments have not been made, no quantitative results are available at the present time, but the following preliminary data will give an idea of the recent work being performed on oxide ore.

	GOLD, OUNCES	SILVER, PER CENT.	LEAD, PER CENT.
Kiln feed.....	0.035	11.4	4.7
Calcine.....	Tr.	1.2	0.2
Fume.....	0.30	64.0	27.8

Tonnage rate to kiln, 7 tons per hr.

Coal consumption, approximately 30 per cent. of furnace feed.

DISCUSSION

T. VARLEY, Salt Lake City, Utah (written discussion).—The development and installation of this process are the outgrowth of the old chloridizing roasting process, supplemented by leaching, that has been carried on on this continent since 1557, as recorded by John Percy and other pioneers of a later date. The history of chloride volatilization, which was the second step in the development of the process, is recorded in Bulletin No. 211 of the U. S. Bureau of Mines and contains details of experimental work by this process on practically every type of ore.

The process outlined in this paper, which eliminates the use of salt in the volatilization process, is well worth favorable comment. The Bureau of Mines began experimental work on this process in 1915 and pursued it rather vigorously until 1922, when the work was considered practically finished from an experimental standpoint. It is, however, only by the application of developed laboratory processes on a commercial scale that discoveries similar to those made in this plant are possible.

The early history states that in many cases, during chloride roasting, large losses of metals such as gold and silver by volatilization were noted and every precaution was taken to eliminate such losses. It was not until about 1893, however, that Pohle and Croasdale discovered important losses in gold and silver tellurides in the Aspen district in Colorado. Experimental work by them proved that the losses were very high, for which reason they decided that if there was a loss under normal conditions that if these conditions were properly adjusted all the valuable materials could be volatilized and subsequently recovered in a highly concentrated form. In their experimental work along these lines, they proved that it was possible to volatilize gold, silver, lead, copper, and other metals, but the process was not successful because it was not possible to collect the fumes in bags or other devices. The process, therefore, was practically abandoned until 1916, when the Bureau of Mines, independent companies, and individuals pursued this investigation. With the advent of the Cottrell electrostatic precipitators, the process was revived, such a means of precipitating the fumes proving satisfactory, and three semi-

commercial plants were installed—one in Idaho, one in Mexico, and one in Arizona. However, because of certain mechanical difficulties these plants were operated only in an experimental way.

The recovery of silver in the Chief Consolidated plant at Eureka is much higher without the addition of salt as a chloridizing reagent. Experimental work on high-grade silver ores has proved conclusively that calcium chloride is a much better chloridizing reagent than ordinary salt, but the high cost of this reagent, in some cases, makes its use prohibitive.

The oxide volatilization of silver, lead, and gold in the Chief Consolidated ores brings up a question of just what are the proper conditions for oxide volatilization of these metals: Are the constituents in the ore just right for desirable chemical reactions to take place and would such reactions take place with any ordinary silver ores? Is there any remaining sulfur in the ore, which acts as a carrier for the valuable metals, or do they volatilize and subsequently pass off as the oxides of the various metals without any reagents that take the place of chlorine in the chloride volatilization process?

Can the author give any figures on the ratio of concentration, taking the weight of the furnace feed as 100 per cent.

S. G. OLMSTEAD, Eureka, Utah.—The feed to the kiln represents approximately 60 per cent. of the feed to the wet plant; at the volatilization plant the fume will run 15 to 16 per cent. insoluble, which with the metal contents constitutes the whole. The concentration ratio will vary between 4 and 10 to 1, depending on the tenor of the feed.

V. O. LAWTON, Salt Lake City, Utah.—How are the metals volatilized? What chemical formula would represent them?

S. G. OLMSTEAD.—We do not know definitely. I believe that the lead comes off in the metallic form and as lead sulfide; in other words what sulfur is present combines with the lead in the fume. The silver comes off in metallic form. Gold is volatilized but in what form is unknown. In the precipitated fume, it is in metallic form.

O. C. RALSTON, Berkeley, Calif.—I believe that I can present a very shrewd guess as to the form the metals are in when they are caught in the fume. The silver can be volatilized in the kiln at a temperature of about 1300° C. without the presence of any chlorides. Published data on the vapor pressure of silver show that at 1300° C. the amount of gas passing through the kiln is more than enough to evaporate all the silver from the ore. As most of the silver minerals on roasting are converted to metallic silver and as the vapor pressure of silver is ample to explain its evaporation, this success of the Tintic Standard volatilization kiln is not difficult to understand.

The volatilization of the lead in the ore is easier to explain. Lead carbonate is converted to lead oxide at a very low temperature and lead sulfide is roasted to lead oxide and lead sulfate. Lead oxide can be evaporated at a temperature as low as 800° in a current of gas, such as passes through this kiln, and lead sulfate is dissociated thermally at temperatures above 1000° , giving lead oxide and oxides of sulfur. Lead sulfate itself is quite volatile at 1300° C. There is therefore nothing mysterious about the volatilization of lead. Of course when the gases are cooled some of the oxides of sulfur can recombine with the lead oxide and then appear in final form as a mixture of lead oxide and lead sulfate.

It is interesting to note that this method applies mainly to finely divided material not too high in lead. The portion of the lead and silver that is easily recovered by gravity concentration is difficult to treat by volatilization and vice versa. Therefore the combination of gravity concentration and volatilization amounts to fitting two processes together, each of which makes up for the disadvantages of the other.

It might be well to point out that an ore which can be heated to 1300° C. without serious sintering or slagging is unusual, and as volatilization without salt cannot be carried on successfully below this temperature, for ores that are more easily sintered chloride volatilization would be necessary; this, of course, can be obtained by simply adding salt to the charge fed into the kiln.

Method of Unloading Ores and Coarse-crushing Practice at Magna Plant of Utah Copper Co.

By B. E. MIX* AND L. M. BARKER,† SALT LAKE CITY, UTAH

(Salt Lake City Meeting, September, 1925)

THE present methods of unloading ore and coarse-crushing at the Magna plant of the Utah Copper Co. are the developments of the past five years. Hand dumping and breaking have given way to the rotary car dump and large gyratory; and the bucket elevators and stationary screens have been replaced by conveyors and shaking screens.

The coarse-crushing plant may be broadly divided into two units: the primary crushing and the secondary crushing, or primary roll, unit. The former was erected in 1923; with the exception of the excavation, the construction was carried on by forces of the company. Excavation was started in the middle of March, the first concrete was poured July 16, erection of the steel building started Oct. 30, and the unit was completed and operating Dec. 30. The unit has a capacity of over 24,000 tons of ore per day, and cost more than a million dollars. Remodeling of the primary-roll unit extended over a period of years preceding this, some of the work having been done as early as 1918.

DELIVERY OF ORE FROM MINE, YARD STORAGE, AND HANDLING ORE CARS TO AND FROM PRIMARY CRUSHING PLANT

The ore is transported, in steel cars of 80 tons capacity, from the mine to the mill, where a reserve tonnage of loaded cars is maintained. Mallet locomotives, handling trains of 45 cars, or approximately 3600 tons of ore per train, deliver the trains to a storage yard which contains three tracks—a passing track and two storage tracks. All of this trackage is equipped with an overhead trolley system, so that electric locomotives can be used in yard switching.

The storage tracks have a total length of 4500 ft. and provide storage space for 140 cars. The passing track, besides permitting switching room for locomotives, is used for storage purposes between train arrivals; thus giving intermittently a total storage capacity for the yard of approximately 200 cars. The amount of ore stored at any one time, however,

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† Metallurgical Engineer, Utah Copper Co.

varies from 25 to 150 cars, or from 2000 to 12,000 tons, depending on rate of train arrivals and mill consumption.

The ore is drawn from the storage yard by electric locomotives, in trains of 10 or 12 cars, and delivered to the primary crushing plant for dumping. Steam locomotives were used in this service prior to this year; but by the use of electric locomotives marked reductions in operating and maintenance costs have been effected. The locomotive switches the loads to a track which leads to the car dumper and connects with empty or make-up yards beyond. When dumped the empty cars are switched to the empty yards, which contain three electrified tracks with a total length of 6700 ft., or sufficient space for 200 empty cars. The tracks descend from the dumper on a gradually reducing grade—3 per

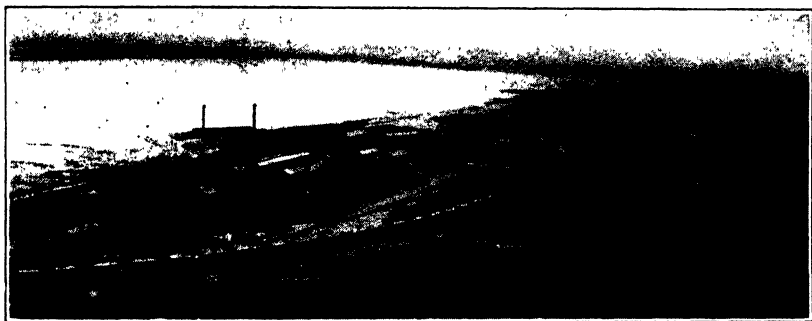


FIG. 1.—GENERAL VIEW OF MAGNA PLANT, LOOKING EAST.

cent. at the dumper but reduced to 1 per cent. in the lower yard—thus permitting placement and switching of empty cars by gravity. In this yard, trains are made up for the return to the mine. A train crew of four men accomplishes the above switching. Two such crews are used in the summer months and three in the winter to maintain a medium tonnage; for maximum tonnage, three crews would be necessary all the year round.

DUMPING, PRIMARY SCREENING, STORAGE, AND INITIAL CRUSHING

Dumping and primary screening and crushing constitute the initial steps in the coarse-crushing operation. The loaded cars, drawn from the storage yard, are switched, two at a time, on to the dumper by the train crew. The dumper, which is of the tandem-rotary type, is composed of two units, which may be operated separately or together; each unit handles one car. This arrangement, besides affording means of varying the dumping rate, assures constant operation when required, facilitates repairs, and minimizes delays. These factors are of particular importance during the winter months when frozen ore must be contended with. Each unit of the dumper is driven separately by a 50-hp. motor

through gear reduction, provision for tandem operation of the two units being made in the electrical control equipment in the operator's cab. Dumping procedure is as follows: Two cars of ore are spotted on the dumper and cut loose from the rest of the train by the train crew. The dumper then revolves these cars 165° , dumping the ore upon a bank by which it is diverted over grizzlies. The bank is composed of ore from previous dumpings. Its use eliminates excessive grizzly wear, and the undue loading of the grizzlies that would result should the ore be dumped directly on them; and it provides for better distribution of the ore over the grizzlies so that more efficient separation of undersize results. The dumpers operate on a 2-min. cycle, but the average time required for the entire operation of spotting cars, etc., is approximately 5 min. This is equivalent to a dumping capacity of 24 cars per hour, or 1920 tons of ore. This is practically twice the maximum daily tonnage required and assures delivery of sufficient ore from the dumpers for the mill demands.

The grizzlies surmount a storage bin of 1500 tons live capacity, and discharge at the mouth of a No. 27, 54-in. gyratory crusher. They consist of two sections, one under each dumper. These sections are car width, 20 ft. long, set at an angle of 42° , and are built up of individual 20-in. T beams spaced $6\frac{1}{2}$ in. apart. The T beams are capped with specially designed manganese-steel wearing plates. Undersize, $-6\frac{1}{2}$ in. ore, passes through the grizzlies to the storage bin, and oversize goes to the crusher. Of the ore dumped, it is estimated that approximately 25 per cent. is oversize and constitutes feed to the No. 27 crusher.

The No. 27 crusher reduces the oversize to $-6\frac{1}{2}$ in. and discharges it to two small bins or crusher pockets. The crusher is a 54-in. double-discharge gyratory, and is driven by a 250-hp., 300-r.p.m. motor coupled direct to the pinion shaft through a specially designed flexible coupling. This consists of two cast-iron halves and a disk made from 12-ply conveyor belting. The disk is connected separately to each half by bolts, the circle of which, for one half, is larger than that for the other. This type of flexible coupling is used primarily for the protection afforded the crusher against tramp iron; in addition there is an overload release on the motor. The crusher pockets are adjacent to the undersize storage bin, and ore can be drawn into them through holes in the partition wall common to both.

DELIVERY, CONVEYING, SCREENING AND SECOND STAGE OF CRUSHING

The ore in the undersize storage bin and crusher pockets is removed by 72-in. pan feeders, which discharge on to belt conveyors. The pan feeders, four in number, are arranged in pairs on opposite sides of the crusher. Of each pair, one feeder is located under the storage bin and the other under a crusher pocket. Two 54-in. belt conveyors are located

directly below the feeders, one to each pair, and take the discharge from them. The storage-bin feeders are driven by two speed motors through reduction gears. The controls for the motors are tied in with the controls of the belt conveyors, thus providing for starting and stopping of feeders and conveyors simultaneously. The feeder motors can, however, be permanently cut out by push-button switches on the control panel if occasion requires. The crusher-pocket feeders are driven by roller chain and sprockets through a friction clutch from the belt-conveyor drive, thus giving operating conditions comparable to those prevailing on the storage-bin feeders. These latter feeders discharge on to a short grizzly, which screens the fine ore on to the belt conveyors and forms a cushion to protect the belts from snagging by coarse ore. The crusher-pocket feeders discharge directly on to the belt conveyors, but subsequent to the discharge of the storage-bin feeders.

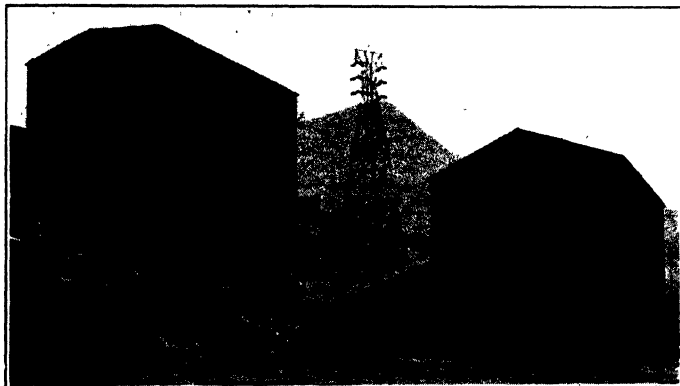


FIG. 4.—CAR DUMPER BUILDING AND NO. 9 CRUSHER BUILDING.

The two 54-in. belt conveyors advance the ore to another unit, known as the No. 9 plant, for the second stage of coarse crushing. These conveyors are operated on a 19° incline, and each is driven by a 125-hp. two-speed motor through double reduction gears and a modified snub drive. Both conveyors are equipped with ball-bearing troughing and return idlers. The motors are equipped with solenoid brakes, which operate on a brake drum attached to the rotor shaft. The brakes automatically release when the motor is started and set when the motor stops, thus preventing backing up of the conveyor when stopped under load. Push buttons for motor control are installed at both the head and the tail ends of conveyors. That at the tail end can be used only for stopping the conveyor, the main control being at the head-end station. The conveyors can be operated at either of two speeds—175 ft. or 350 ft. per min. This provision is made primarily so that the maximum ton-

nage of ore can be handled by one belt should occasion require it. The conveyors discharge the ore into a steel hopper in the No. 9 plant, at which point tramp iron and mine timber are removed from the ore by an operator stationed there for that purpose.

From the steel hopper, the ore is discharged over four grizzlies whose product, undersize and oversize, are diverted to a surge bin and four gyratory crushers, respectively. The grizzlies and crushers are located in pairs on opposite sides of the hopper. The hopper is supported on a steel structure over the grizzlies and serves merely as an ore distributor. Flow of the ore over the grizzlies is controlled by lifting counterbalanced swing gates. Stoppage of the feed to one grizzly simply increases the quantity thrown to those remaining in operation. The grizzlies, built up with standard manganese-steel T bars, are 12 ft. long, 6 ft. wide, slightly fanned at the bottom, and set at an angle of 42° . Spacing of

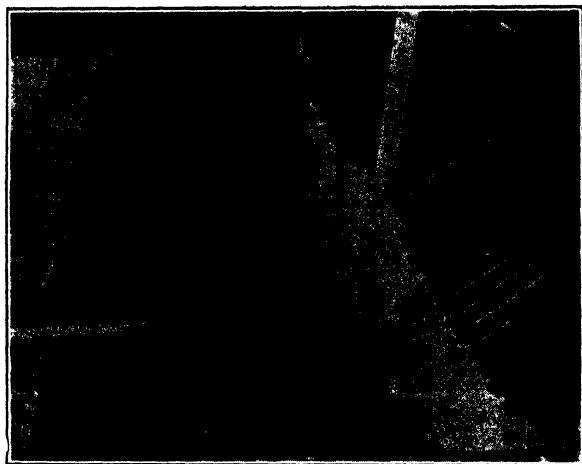


FIG. 5.—GRIZZLIES AND HOPPERS OVER NO. 27 CRUSHER, CAR DUMPER BUILDING.

grizzly bars is varied, to suit ore conditions, within the following limits: in the summer with dry ore, $1\frac{1}{4}$ in. spacing; in winter and early spring with wet and frozen ore, $2\frac{1}{2}$ in. spacing. Of the tonnage of ore delivered to the grizzlies, approximately 30 per cent is oversize and is discharged into the No. 9 crushers. These crushers are of the short-head type and are direct driven through a flexible coupling of the same design as used on the No. 27 crusher drive, by a 125-hp. 450-r.p.m. motor. In addition to the normal control equipment at each motor, push-button cut-outs are installed on the hopper or operating floor. Each crusher is equipped with force-feed oil pump for lubrication of eccentric bearings and cold-water coils for maintaining the lubricating oil at a moderate temperature. There is also provided an external pumping and filtering system for continuous treatment of the oil circulating in all crushers.

The crushers reduce the oversize from the grizzlies to approximately $-2\frac{1}{2}$ in. and discharge their product to the surge bin where it joins the grizzly undersize.

All of the equipment described so far is contained in one building, which practically consists of two parts. One contains the dumping plant, bins, feeders, and No. 27 crusher, and the other, the No. 9 plant, with its grizzlies, No. 9 crushers, and surge bin. In both plants most of the operating floor space is below ground level. The building is constructed of concrete and steel and provided with sufficient windows for good lighting. In its design, care was taken to provide ample room around

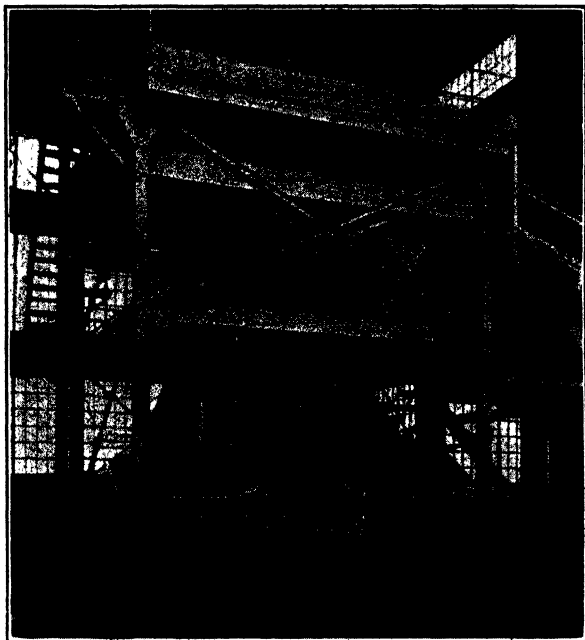


FIG. 6.—HOPPER OVER CHUTES AND GRIZZLIES FEEDING NO. 9 CRUSHER.

all equipment, so that it would be easily accessible and safe for operating and repair crews. Guard rails and screens have been provided, wherever possible, around all dangerous places, and stairways and runways were made of ample width. The dumping plant constitutes the main portion of the building and contains four floors. The vertical distance from the car-dumper track, or first floor of the building, to the bottom floor is 97 ft. This part of the building is equipped with a 60-ton electric crane, having a 10-ton auxiliary hoist. This crane serves directly all heavy equipment, except pan feeders and tail pulleys of belt conveyors. Manual labor is reduced to the minimum in handling such equipment, however, as a shaft 8 ft. square extends from the third to the bottom floor.

Most of the work of replacement, or removal, is accomplished by the crane through this shaft. The No. 9 plant contains three floors, the top floor providing ample rigger space for daily repairs. This part of the building is equipped with a 30-ton electric crane, which can handle directly, or through hatchways, all heavy equipment in this plant. A standard-gage railroad spur enters the building on the third floor. The bottom floors of the two main portions of the building are connected by a tunnel 4 ft. wide and 6 ft. high, which, besides serving as a passageway, is used as a cableway for power lines and for drainage purposes.

DELIVERY TO AND TREATMENT IN THE SECONDARY COARSE-CRUSHING PLANT

Conveying and Weighing of Ore and Removal of Undersize Resulting from Primary Treatment

From the surge bins below the No. 9 crushers, the ore is discharged through chutes to two 54-in. horizontal conveyors, which deliver it to



FIG. 7.—CONCRETE TUNNEL FOR CONVEYORS.

the secondary crushing plant. The conveyors run through a tunnel 23 ft. wide and 325 ft. long. The remoteness of the primary crushing plant from the mill building proper and the presence of Bingham & Garfield R. R. tracks and shops between necessitated the construction of this tunnel and the use of this additional conveying equipment. These conveyors are equipped with ball-bearing idlers, also six sets of conveyor aligning idlers each, equally spaced throughout their length. They are driven from the head pulley by 50-hp. two-speed motors through double-

reduction gears and flexible couplings of the design described. Like the 54-in. incline conveyors, push-button control of the motor is provided, stop buttons being placed at regular intervals along each belt. A signal-light system assists the operators in the coordination of the several units of the primary crushing plant; there, also, two belt speeds are provided for operating contingencies. Recording weightometers are installed near the head end of these conveyors; at this point, also,

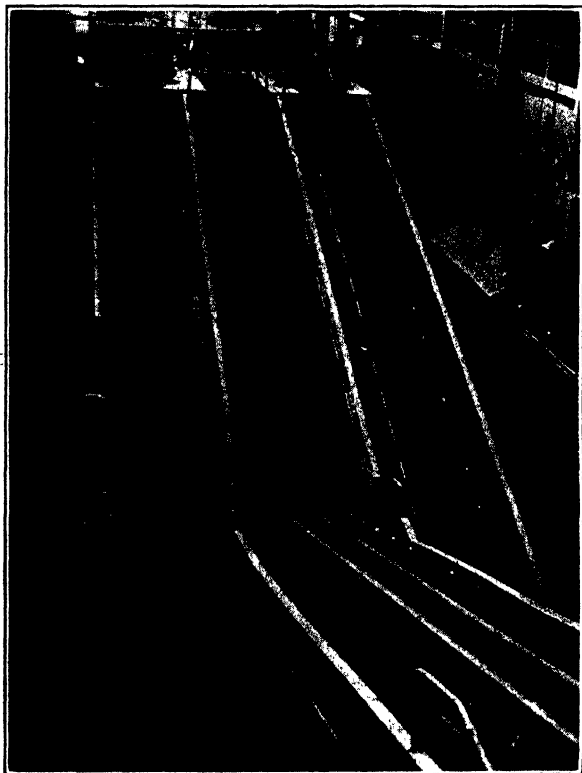


FIG. 8.—CONVEYORS IN PRIMARY ROLL PLANT.

moisture samples are taken from the ore stream. Each conveyor discharges upon a specially designed four-cam impact screen, the under-size of which is diverted to conveyors delivering to the fine-ore storage bins. On these screens, as in the case of the grizzlies, the opening (in this case screen mesh) is varied to meet ore conditions. On dry ore, 1 by 1 in. mesh is used; on wet ore, as large a mesh as $1\frac{1}{2}$ by 3 in. The entire primary coarse-crushing plant tonnage is treated by these screens, and of this tonnage approximately 60 per cent. is oversize. This over-

size discharges into a surge bin, which feeds two short 48-in. belt conveyors delivering to the secondary crushing, or primary roll plant.

Primary Roll Grinding and Accessory Screening and Conveying Equipment

The primary roll plant contains two similarly equipped units, each of which receives ore from one of the 48-in. conveyors. The ore is discharged upon a 48-in., 21° incline, belt conveyor, which delivers it to a hopper above two 72 by 20-in. rolls. The conveyor is equipped with ball-bearing troughing and return idlers, and is driven by a 100-hp., 690-r.p.m. motor through a flexible coupling, reduction gears, and

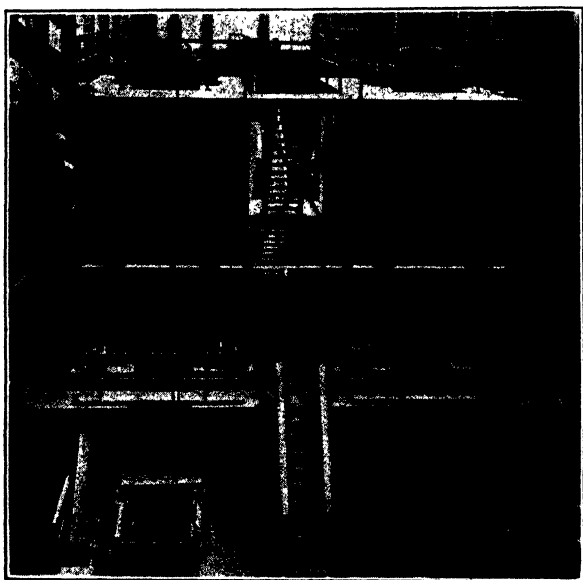


FIG. 9.—SCREENING TOWERS IN PRIMARY ROLL PLANT.

tandem drive, at a speed of 420 ft. per min. The hopper above the rolls is two-way and provided with a basket-type splitter gate, so that feed to either roll can be cut off and diverted to the other roll when necessary. Construction of the hopper is such that the ore discharged into it falls upon a bed of ore, thus eliminating the use of liners. From the hopper the ore passes to the two 72 by 20-in. rolls. Each roll is belt driven from a line shaft, which is, in turn, driven through a flexible coupling by a 250-hp. 300-r.p.m. motor. The product of each roll discharges upon a 36-in., 21° incline conveyor, the tail of which is directly beneath the roll. The equipment and drives of these conveyors are similar to those of the 48-in. conveyor, except that the motors are 50 hp. 670-r.p.m., and the belt speed of both is 370 ft. per min.

The 36-in. conveyors each discharge into a round-bottom, steel, surge bin, or screening tower, from which the ore is drawn by drum feeders, of which there are four, in pairs, under and on opposite sides of the bin, 36 in. in diameter and 72 in. long. The tonnage delivered from them is regulated by adjustable swing gates. The impact screens are of special design, two cam type, and mounted one under each feeder. Two cam shafts, belt driven by a 5-hp. motor, operate the four screens. The mesh of these screens is varied with ore conditions, but is seldom greater than 1 by 1 in. or smaller than $\frac{3}{4}$ by $\frac{3}{4}$ in. The screen undersize constitutes the finished product of this plant and is diverted to conveyors that deliver it, together with the undersize of the four cam-impact screens, to the fine-ore storage bins.

The screen oversize falls upon a 36-in. conveyor, which delivers it to a 54 by 20-in. roll. The drive for this roll is similar to that of the 72 by 20-in. roll, except that appropriate pulleys are included on the line shaft for belt driving the drum feeder mechanism and the 36-in. conveyor of the screening tower. The product from the 54 by 20-in. roll passes through chutes to the 48-in. incline conveyor, thus being returned to the circuit heretofore described.

All of the equipment of this plant, as well as considerable accessory equipment, is contained in one building. Of the accessory equipment, a 30-ton electric crane is the most important. This serves directly, or through hatchways, all heavy machinery in the plant. The building itself contains no unusual structural features.

ADDENDUM

In its broader aspects, the efficiency of a coarse-crushing operation cannot be measured only in terms of tonnage treated and degree of reduction made. The cost of the operation per ton of ore is usually the most important consideration. Some general cost data on Magna's operation are as follows: Average total cost per ton \$0.03904. This cost is made up of the following items:

Operating labor, per ton	\$0.01053
Car dumper, per ton	0.00072
Crushers (No. 27 and No. 9), per ton	0.00294
Feeders and conveyors, per ton	0.00747
Screens, per ton	0.00173
Secondary rolls, per ton	0.00737
Electric power, per ton	0 00828

These costs were obtained when treating a medium tonnage and do not include overhead expense. The reduction accomplished by these crushing operations is from general run-of-mine material to $\frac{3}{4}$ in. size.

DISCUSSION

W. C. MADGE, Salt Lake City, Utah.—What is the speed of the conveyors?

B. E. MIX.—There are two conveyors in each unit, both running normally at 175 ft. per min. If one is stopped for any length of time, the other conveyor is speeded up to 350 ft. per min. to carry the total tonnage during the time the one is idle.

Mechanism of Filtration

BY ARTHUR W. HIXSON,* LINCOLN T. WORK* AND ISAAC H. ODELL, JR.*

(New York Meeting, February, 1926)

ALTHOUGH a few engineers have recognized the problem of the mechanism of filtration it has never been studied in a quantitative way. A background for a better understanding will be afforded by a survey of certain fundamental principles of filtration.

In recent years, authorities have become practically unanimous in saying that the actual filtering should be done, not by the cloth itself, but by a layer of solid particles deposited upon it. Thus, a cloth may be used in which the openings are considerably larger than the particles to be filtered, provided that groups of particles form an arch or bridge over each opening. This can be accomplished if the initial pressure is so low that the arch will not be broken while it is still thin. According to Wright,¹ the chief advantage of this method of filtration is that the open-weave cloth does not become clogged as easily as does one of closer weave, where the fine particles often work their way into the interior of the cloth and become caught there. If the character of the material to be filtered is such that it will not form a good film, then it becomes advantageous to use "filter aids" for pre-coating the cloth with a desirable layer of solids, and the coating need be only of a very slight thickness for good results. Until the film is formed, the first runnings of the filtrate may be cloudy, often necessitating refiltering this portion.

A factor which has considerable effect on the performance of filters is the concentration of solids in the pulp. According to Wright, a high concentration of solids gives a porous cake, since the flow is then slower than with a thin pulp. The porosity of the cake is also affected by the pressure: a high initial pressure tends to compact the cake, and the same effect results from fluctuations of pressure. In his studies of the relation between pore size and particle size, Hatschek² observed that the particles in a pulp tend to arrange themselves with maximum cross-section parallel to the direction of flow and that this is more marked at the higher velocities. Thus, at high pressure and high velocity, a certain pulp

* Dept. of Chem. Eng., Columbia Univ.

¹ A. Wright: Industrial Filtration (1923).

² E. Hatschek: Mechanism of Filtration. *Jnl. Soc. Chem. Ind.*, (1908), **27**, 538. Principles of Technical Filtration. *Jnl. Soc. Chem. Ind.* (1920), **39**, 226-8T.

will pass through a given filter cloth, whereas, at a lower pressure and a correspondingly lower velocity, a cake will be built on the cloth.

The researches on plasticity by E. C. Bingham,³ while they do not concern filtration directly, do suggest a new approach for the study of the problem. Bingham investigated the flow of suspensions of clay in water, and also of paints in oils, using capillary tubes considerably larger than the particles of the material. He notes, that, when the force applied is only slightly greater than that necessary to start motion, a condition of seepage exists, with the liquid being forced through the pore spaces between the solid particles. Other things being equal, this effect becomes greater as the size of the capillary decreases. It would therefore seem that a size of tube could be reached at which this seepage effect would be great enough to produce filtration.

SIZE OF PARTICLES AND OF FILTER OPENING

An experimental study was made to determine the relation between the size of particles and the maximum possible size of filter opening, using calibrated capillary tubes for the openings. The material used was quartz sand, previously ground in a ball mill. This was screened to mesh intervals of 130-230, 230-325, and minus 325, the sizes being designated respectively as (1), (2), and (3). The last was further classified by the method of sedimentation, and three fractions designated respectively as (3-a), (3-b), and (3-c) were obtained. All of these were examined microscopically, the intermediate dimension or the short diameter in the plane of the microscope being taken as the criterion of size. The five fractions finally obtained were of the following sizes:

- (1) .085 — .165 mm.
- (2) .060 — .085 mm. (3-a) .030 — .060 mm.
- (3) .000 — .060 mm. (3-b) .012 — .030 mm.
 | (3-c) .000 — .012 mm.

From sizing data, it was determined that (3) contained 40 per cent. of (3-a), 15 per cent. of (3-b), and 45 per cent. of (3-c).

The tubes used for filtration were made by drawing out thick-walled 1-mm. glass tubing. Their diameters were determined with the microscope to a precision of about .010 mm. The sizes of those tubes which affected the results were .160, .208, .264, .340, .392, .464, .496, .560, and .624 mm. For convenience, these figures will all be expressed as microns, .001 mm. equalling 1 micron. The filtrate from the capillary tube was received in a glass bottle connected through a stop-cock to the capillary. The receiver was connected to a vacuum vessel which had outlets to the vacuum pump, the manometer, and the atmosphere.

³ E. C. Bingham: *Fluidity and Plasticity* (1922).

Each pulp was prepared in a small beaker, into which the capillary was dipped, and the vacuum was gradually applied by closing the outlet to atmosphere. If a cake formed, the vacuum was increased to 25 in. of mercury, to determine whether the cake would withstand this pressure. Several attempts were made before recording a negative result. This procedure was followed with each of several capillaries to locate the limit, which was taken as the smallest size of capillary upon which no cake would form. Where cake formation was very difficult with one size of tube, or the cake broke down before full vacuum was reached, the result was recorded as doubtful between two tube sizes. But, as such cases were not numerous, the precision with which the limits were determined may be considered to be about 30 or 40 microns. In this manner, the maximum filter opening was determined for a variety of particle sizes and pulp densities.

MICROSCOPIC EXAMINATION OF CAKE

Several representative cakes were removed from the capillary and examined under the microscope. In the center of each cake, there was an arch in which the larger particles formed the structure. This arch evidently acted as the support for the entire cake, and the interstices in it formed the ducts for the passage of the liquid. A typical section of the cake is best shown by a sketch, as in Fig. 1.

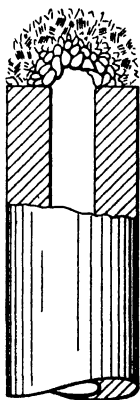


FIG. 1.—STRUCTURE OF FILTER CAKES.

The results, which are shown graphically in Figs. 2 to 6, may be summarized as follows:

1. For a narrow range of particle sizes, the limiting size of filter opening is essentially constant from a pulp density of 60 per cent. down to 15 or 20 per cent. Below this percentage, the opening is less, approaching the size of the largest particle in the sample as the solid content approaches zero. Under the condition that the particles are infinitely

RELATION BETWEEN MAXIMUM FILTER OPENINGS, PARTICLE SIZE AND PULP DENSITY

Fraction Number	Particle Size, Microns	Pulp Density, Per Cent. Solid	Maximum Opening, Microns	Blend Number and Per Cent.	Pulp Density, Per Cent. Solid	Maximum Opening, Microns
(1)	85-160	60	624	(1)-(2) 50%-50%	60	624
		40	624		40	624
		20	624		20	624
		10	560		10	560
		5	496		5	496
		2.5	464			
(2)	60- 85	60	560	(1)-(2) 25%-75%	58	624
		40	560		40	624
		20	560		20	560 (624)
		10	496		10	496
		5	464		5	464
(3) 40% <i>a</i> -15% <i>b</i> 45% <i>c</i>	0- 60	60	464 (496)	(1)-(2)-(3) 50%-10%-40%	60	624
		40	496 (464)		40	624
		20	464 (496)		20	560
		10	392 (464)		10	464 (496)
(3- <i>a</i>)	30- 60	60	464 (496)	(1)-(2)-(3) 25%-25%-50%	58	624
		40	496		40	560 (624)
		20	496 (464)		20	496
		10	496 (464)		10	392
		5	392			
		2.5	392	(1)-(2)-(3) 10%-10%-80%	60	624 (560)
		1.6	340		40	496
					20	464
					10	392
(3- <i>b</i>)	12- 30	50	464	(2)-(3) 20%-80%	60	496 (560)
		38	392		40	496 (560)
		20	392		20	392
		10	392		10	392
		5	340			
(3- <i>c</i>)	0- 12	57	340	3(<i>a</i>)-(<i>b</i>)-(<i>c</i>) 10%-10%-80%	57	464
		40	340		40	464 (392)
		20	340		20	392
		10	340 (264)		10	340
		5	208			

far apart, each one would come to the opening separately, and the largest particle would start filtration in any tube of less than its own diameter.

2. There is a definite mathematical relation between particle size (*P*) and filter opening (*C*) in microns for sized fractions of greater than 20 per cent. solid content. Using the maximum particle size in the sized fraction, the relation is $C = 175 \sqrt[3]{P_{\max}}$. Using the average particle

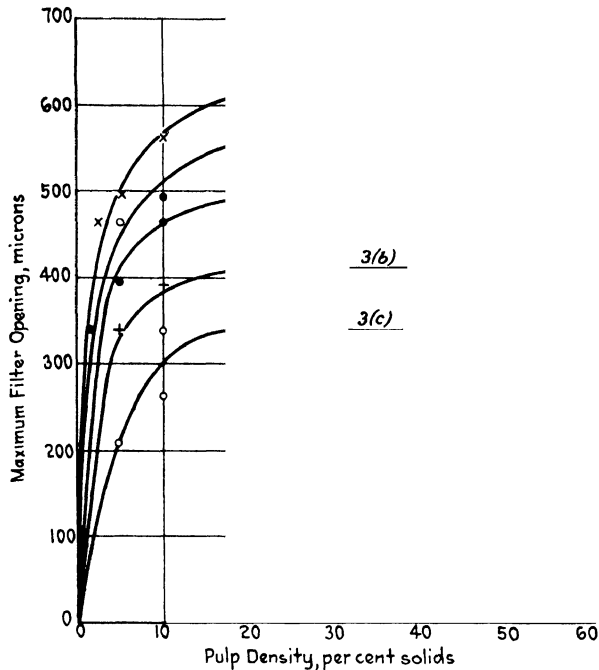


FIG. 2.—COMPARISON OF PULP DENSITY AND MAXIMUM FILTER OPENING FOR PARTICLES IN NARROW RANGES OF SIZE.

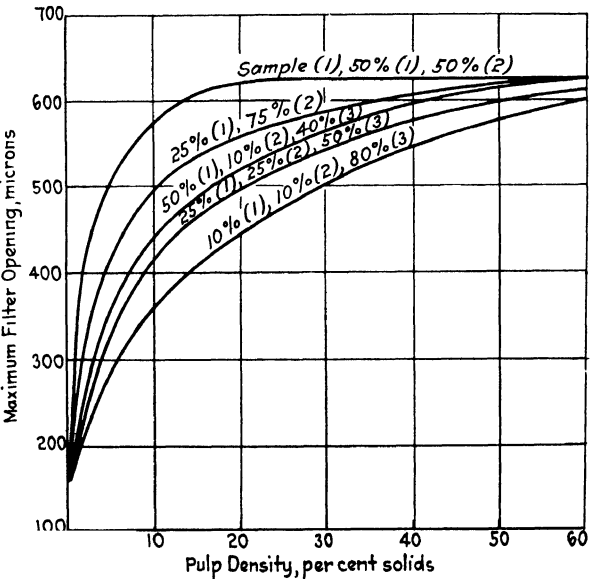


FIG. 3.—COMPARISON OF PULP DENSITY AND MAXIMUM FILTER OPENING FOR BLENDS OF SIZED PARTICLES.
Sample (1) as maximum size.

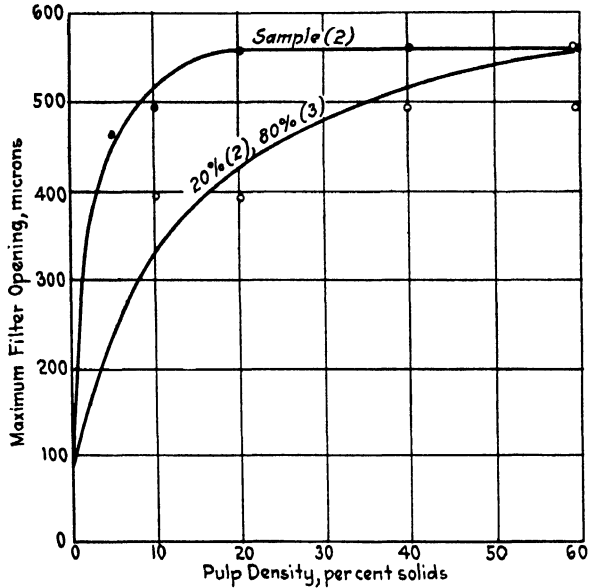


FIG. 4.—COMPARISON OF PULP DENSITY AND MAXIMUM FILTER OPENING FOR BLENDS OF SIZED PARTICLES.
Sample (2) as maximum size.

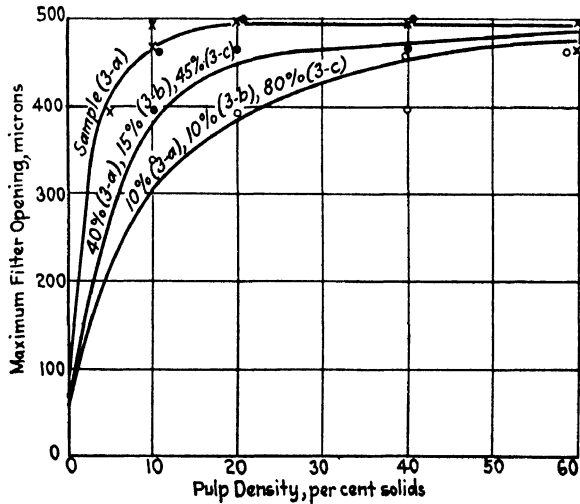


FIG. 5.—COMPARISON OF PULP DENSITY AND MAXIMUM FILTER OPENING FOR BLENDS OF SIZED PARTICLES.
Sample (3-a) as maximum size.

diameter, it is $C = 190 \sqrt[3]{P_{av}}$. Both equations are equally applicable, and there is at present no reason for selecting one in preference to the other.

3. In blended samples formed by the substitution of finer particles for a portion of the sized fraction, the fall in the value of the filter opening occurs at a higher pulp density and it is more gradual.

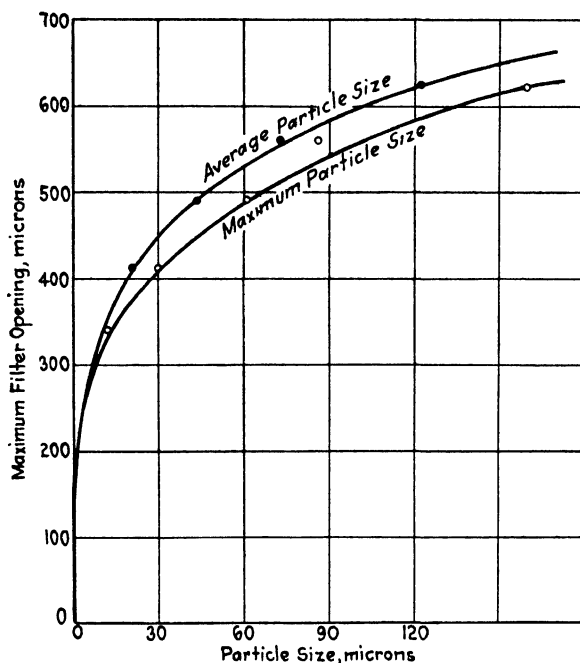


FIG. 6.—COMPARISON OF PARTICLE SIZE AND MAXIMUM FILTER OPENING. (20 TO 60 PER CENT. SOLIDS.)

FURTHER SIGNIFICANCE OF DATA

When studied and interpreted, the data have still further significance. For instance, it is conceivable that each size of particle might play its proportionate part in determining the maximum size of filter opening. Thus, if the effect of each single interval of size in a blended sample were proportional to its percentage in the blend and to its maximum filter opening when alone, it would be possible to predict the maximum opening upon which the blend would filter at any pulp density. For example, curve *c* (Fig. 3) shows a sample containing 50 per cent. of size (1), 10 per cent. of (2), and 40 per cent. of (3). At 10 per cent. solids in the pulp, the filter openings for (1), (2), and (3) are 565, 515, and 375 microns, respectively. These values are taken from the curves. On this basis, the value of the maximum filter opening for the blend

in 10 per cent. concentration in the pulp should equal $.50 \times 505 + .10 \times 515 + .40 \times 375 = 483$. The value from curve *c* is 445. These relations hold fairly well, within the precision of the determinations, in the lower concentrations; but above about 40 per cent. solids the calculated values are considerably lower than the experimental ones. In high solid concentrations, therefore, the constant which represents the effect of a given range of particle sizes in a blended sample must be greater than the filter opening corresponding to that particle size when isolated. Fig. 7 shows a set of constants which can be used to calculate the filter opening for a given pulp density of a given blend of particle sizes. The results so obtained agree with the experimental data within the precision

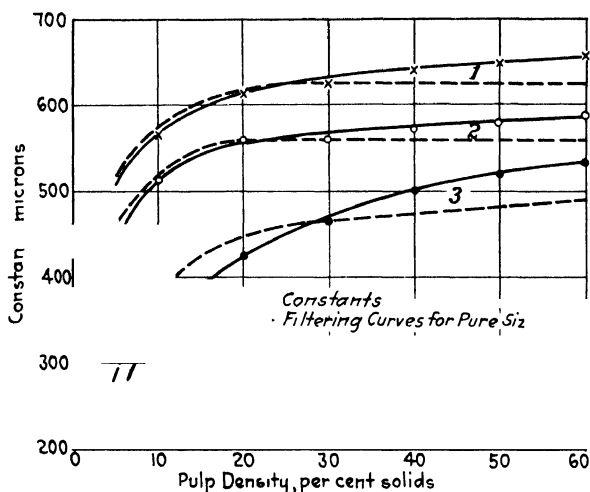


FIG. 7.—CONSTANTS FOR EFFECT OF EACH SIZE.

of the determinations. Since these constants do not differ greatly from the values for the sized fractions it is possible that the curves for the latter are not truly horizontal above 20 per cent. solids, but that they rise with the pulp density by an amount not detected in the experiments.

CONCENTRATIONS OF SOLIDS AND PARTICLE ARRANGEMENT

It is also probable that, at high pulp densities, there is a condition which renders cake formation easier than in more dilute pulps. High concentration of solids may affect the particle arrangement, in that there will be less tendency in the thicker slurries for particles to arrange themselves with their greatest cross-section parallel to the direction of flow. Moreover, the finer particles when close together may have more tendency to take part between the larger ones in the filter bridge formation, thus increasing the diameter of the bridge. In other words, with thick

pulps, the combined action of the various sizes may be greater than the sum of their separate actions.

There is also the possibility that the maximum filter opening for any pulp is determined by the actual concentration of the particles of maximum size in the total weight of the pulp. This is indicated by the fact that, for all samples having the same percentage of size (1) in the total weight of pulp, the filter opening is nearly constant, varying in no case by more than one capillary size interval. A similar condition exists in samples with (3-a) as maximum size. This suggests that the frequency with which the particles of maximum size occur is the determining influence, but it is hardly conclusive. That the larger particles of a mixture play a predominant part in the formation of the filter bridge is shown by the results of microscopic examination of the cakes, as well as by the experimental results.

So far it is impossible to state which of the two factors determines the size of opening on which a given pulp will filter. In the case of the thicker pulps of the blends, the facts favor the idea of concentration of maximum particles, while, with more dilute suspensions, each band of sizes seems to have an effect proportional to its own size of filter opening.

AS PARTICLES BECOME SMALLER LARGER NUMBER FORM BRIDGE

An interesting fact is brought out in connection with the ratio between capillary size and particle size, shown in Fig. 8. It is an axiom in the design of apparatus for handling materials in bulk that all gates and orifices should be at least three times the size of the largest pieces present, because three particles will form a bridge and clog the opening. The figure shows that the ratio between opening and particle size approaches this value of three in the largest sizes. The curve has a value of four for size (1) and it seems to be asymptotic to a value of three for still larger sizes. But the ratio increases rapidly as the particles become smaller, being about 28 for size (3-c). Thus, as the particles become smaller, a larger number of them will form a bridge. It would seem as if the viscous resistance of the thin fluid films between particles contributed largely to the increase of this ratio. A full explanation of the theory of this phenomenon not only would aid in explaining bridge formation at the filter opening but also would go far toward an understanding of the resistance of filter cakes to fluid flow.

The results obtained with quartz can not necessarily be applied quantitatively to materials with particles of different shapes or of still smaller sizes, but the general tendencies will probably apply in all cases. The form of the curves and the effects of blending sizes should be much the same for any material. Other factors which would be likely to affect the results are the shape of the openings and their distance

apart. The use of square, oblong, or irregular holes, instead of round ones, would change the conditions of bridge formation. The presence of adjacent openings would alter the directions of fluid flow into any given orifice and this, too, would affect the bridge formation.

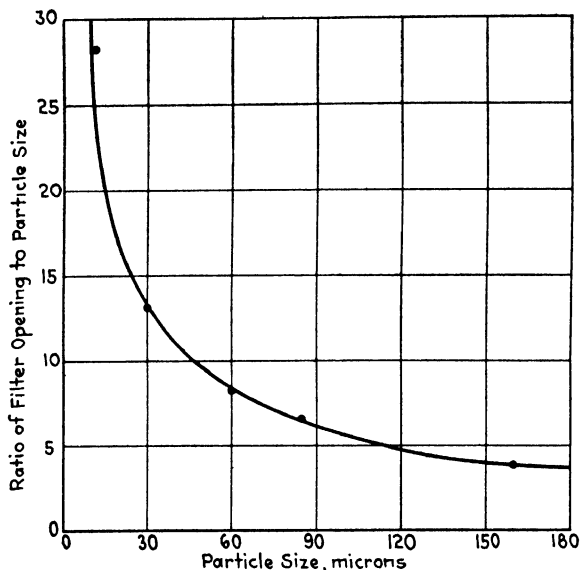


FIG. 8.—RATIO OF PARTICLE SIZE AND FILTER OPENING FOR EACH RANGE OF PARTICLE SIZES. (20 TO 60 PER CENT. SOLIDS.)

USE OF THICK PULPS DESIRABLE

While the conditions existing in these experiments differed from those encountered in filtration practice, the data are sufficiently definite to justify practical suggestions. Probably the most striking fact is the desirability of using as thick pulps as can be conveniently handled. By this means it becomes possible to use a filter medium with larger openings, thus gaining the advantages mentioned by Wright and others, such as, better flow and absence of clogging. To achieve the same end, the pulp should be of a suitable degree of fineness, or, if it is already too fine for ready filtration, it should have coarse "filter-aid" added. In a general way, these things have been known. This paper offers a method of making more quantitative the selection of a proper filter medium.

DISCUSSION

J. A. BAKER, Newfield, N. J.—Mr. Work, have you made any observations on the effect of the amount of vacuum on the structure of cake?

L. T. WORK.—The vacuum was always maintained at a low value to start. In certain cases, if the vacuum was initially very high, the cake

would not form on a large capillary, whereas at a low vacuum, it would. As far as the structure was concerned, we noted no differences. We had only a qualitative measure in the microscopic examination. This structure is largely that of cakes formed under a low vacuum first and followed by a high vacuum.

G. H. CLEVINGER, Boston, Mass.—It is well to bear in mind that filtration is brought about by a difference in pressure between the pulp and the filtrate. In the vacuum filter you have the difference in pressure between atmospheric pressure and whatever vacuum is used. In the pressure filter you have the difference in pressure between atmospheric pressure and whatever pressure above atmospheric pressure is used. Often the rather narrow range in pressure difference possible in the vacuum filter is all that is necessary to obtain the most economic results. At one time it was thought that greatly increased capacity could always be obtained with pressure filters because of the greatly increased difference in pressure that could be had, but with slime containing little granular material this often did not prove to be true. When there is a large proportion of granular material, an increase in pressure difference may, and often does, increase capacity. If these studies had been carried on at still higher pressures, there probably would have been noted compacting of the filter cake with lessening of the rate of filtration.

L. T. WORK.—Your point is well taken, that we should not try to draw the same conclusions for pressure filtration. However, we were studying primarily the action at the filter surface. Under extremely high pressures, distortion of the cloth very often takes place allowing a cake that is once formed to break down.

G. H. CLEVINGER.—At one of the plants where they first introduced vacuum filtration, experiments were made at first with a filter press about 100 lb. per sq. in.; it was hard to get solution through a cake $\frac{1}{4}$ in. thick. With a vacuum filter there was no trouble in forming a cake $\frac{1}{2}$ to $\frac{5}{8}$ in. thick and obtaining a reasonable flow of solution through it. Pressure is rather important, and it has worked out that in metallurgical work at least—the situation may be a little different in the chemical industry—that the vacuum filter, everything considered, appears to have a decided advantage. That is, you do not gain much by increasing pressure.

J. B. PORTER, Montreal, Que.—I have an impression that you can sometimes start with a low pressure and increase it, with less breakdown of the cake than if you started with a higher pressure and kept it up. Mr. Work, have you found that to be so?

L. T. WORK.—Yes.

G. H. CLEVINGER.—The question might be asked where does thickening leave off and filtration begin? Could not some cases be

regarded as thickening problems where actually filtration might be more advantageously applied? Mr. Callow might say something on this subject with particular reference to the Genter thickener, which after all is roughing filter rather than a thickener in the ordinary sense of the term.

J. M. CALLOW, New York, N. Y.—The Genter is a filter thickener in which a filter medium is used to remove the liquid. It is largely used in beet-sugar work but is being gradually extended into metallurgical work. In the first carbonation juices in beet-sugar work, we have pulp containing about 3 per cent. solids. By the use of this filter, we take off 75 to 80 per cent. of the solution in the thickener and thereby relieve the drum filters, which follow, of that much work, so that only about 20 per cent. of the total burden is on the drum filters. This makes a continuous process, as against the old plate and frame presses once used in this business, and they now require only about one-tenth of the filter area formerly used.

Where thickening should stop and filtering commence is a practical question, depending upon the machine used for the final filtering. The drum or disc type of filter requires the thickest possible pulp in order to get proper removal of the cake, so that its capacity depends upon the amount of filtrate to be withdrawn. Therefore, the thicker the pulp the larger the capacity of the machine.

You cannot put upon a drum filter material that runs $3\frac{1}{2}$ per cent. solids, for instance, because the cake would be so thin that you could not possibly scrape it off. With this filter-thickener device, a very thin cake forms on the sacks, sometimes not over $\frac{1}{16}$ in. thick, before it is thrown off. Under these conditions, you get the advantage of that high initial rate of filtration, with which we all are familiar.

G. H. CLEVENGER.—If you start with a pulp having a high ratio of liquid to solids and a pulp of maximum density is required in the discharge, it would seem to be clearly a case for the simple gravity thickener. On the other hand, if elimination of only a small proportion of liquid is required and a clear overflow must be had, it is quite possible that the automatic type of roughing filter may be better because of the small space occupied and the clearer overflow. Such cases may arise in flotation but each individual case requires careful study to determine which type should be used.

J. M. CALLOW.—Probably Mr. Clevenger and I have in mind the same set of experiments that were made on some flotation concentrates—lead, zinc and iron concentrates—in which we wanted to raise the percentage of solids from 25 to 65 per cent. If you use a Dorr tank, where you depend upon sedimentation with 25 per cent. solids, or sometimes

35 per cent., the settling rate is very low and a very large area is necessary because of the density of the initial pulp in the thickener whereas it is really more advantageous to use the filter thickener. This device has a relatively small amount of liquid to remove as against the large amount of solids.

G. H. CLEVINGER.—Briefly stated, when the amount of filtrate to be removed is relatively small, filtration may be advantageous; but when the amount is very large, the gravity thickener should be used to bring the pulp up to the point where the filter can efficiently handle it.

J. M. CALLOW.—If you take a concentrated pulp as it comes off the flotation sheet, say it runs 30 per cent. solids, and put that on a drum filter, the cake is so thin it can hardly be scraped off. Put it through a filter thickener and at the expense of one filter you may be able to save the outlay on two or three drums, and the sum total cost of the filter thickener plus the drum thickener will be very much less than if the drum alone were used. After the preliminary thickening treatment $\frac{1}{2}$ to $\frac{3}{4}$ -in. cakes can be scraped off the drum.

The filter thickener has another advantage in that a high rate of filtration can be obtained with pulps which are carried by liquor of high density, such as zinc sulfate and solutions in zinc leaching plants, whereas the rate of settling with the gravity settling plant is very low.

A. B. PARSONS, New York, N. Y.—Did Mr. Callow say that the Genter filter was thickening from 25 or 30 up to 65 per cent. solids?

J. M. CALLOW.—Yes.

A. B. PARSONS.—Then it is also suitable for thickening up to 30 per cent. It has a double function, is that it?

J. M. CALLOW.—It has, but it is questionable whether it would pay as against a gravity settler. The trouble with the use of gravity settling in the sugar business is the long time of contact in the tank. You get an inversion of the sugar, due to the long time you are in process, whereas you are in and out of process in a Genter thickener in a few minutes. Then too, you are dealing with solutions near boiling, although that should help rather than hinder gravity settling.

With the cold pulps, tailing for instance, where you have 10 to 1, you must take 10 tons of water away from 1 ton of solids. That is putting heavy duty on the filter thickener and in this case the gravity thickeners might show a lower investment cost.

A. B. PARSONS.—How is the Dorr thickener working out, compared with the Genter thickener in metallurgical work?

J. M. CALLOW.—A number of experiments have been made but we have nothing definite to offer as yet. We are putting in another machine

for the Veille Montagne Co. in France, for the same purpose that Traill is using it.

B. R. BATES, New York, N. Y.—When a thickener is fed with 25 per cent. solids the question would probably be more one of volume of the tank than one of area. With a thickener feed in the hindered settling zone, area would probably figure very little. The problem would be retention of that pulp until it reached its final density for discharge.

G. H. CLEVENGER.—It amounts to double filtration when handling lead, zinc and iron concentrate, the Genter thickener doing the roughing and the drum or disc filter doing the finishing. With a middling from flotation when only a little fluid must be removed, only the single operation in a Genter thickener would be necessary.

C. E. LOCKE, Cambridge, Mass.—The flow of pulps through orifices has always been a problem to the millman, that is, to know when an orifice would clog and when it would not clog. It seems to me a study of these arches should have an application in connection with all sorts of small orifice work in milling.

Classification in Witwatersrand Mills

BY BENNETT R. BATES,* NEW YORK, N. Y.

(New York Meeting, February, 1926)

NOWHERE in the world has cone classification in closed-circuit grinding with tube mills reached as high a state of development as on the Witwatersrand. In the development of the Far East section the necessity of fine grinding to obtain satisfactory residues gave rise to a situation with which the cone could cope only at a great sacrifice in efficiency of tube-mill grinding. H. A. White¹ recognized the limitation of the cone in his study of the theory of tube milling as early as 1915, but it was not until Ewing, Davis and Willey² carried out their tests at Springs Mines during 1920 that the advantages of mechanical classifiers were demonstrated.

During the fall of 1924 the writer supervised a series of tests with Dorr classifiers undertaken by Mr. White, Consulting Metallurgist, at the mill of the Geduld Proprietary Mines, Ltd., Dersley, Transvaal (Far East Rand). The importance of classification to obtain efficient tube-mill grinding was thoroughly demonstrated. The installation of classifiers of the above type that followed the test confirmed the results of the experimental work.

TESTS WITH CONES, STRAIGHT TYPE AND BOWL CLASSIFIERS

The test at the Geduld mill was made to determine the relative grinding efficiency of a tube mill when grinding in closed circuit with cones, straight type Dorr classifier and Dorr bowl classifier. The efficiency of a tube mill, as expressed in this article, is based on the tons of minus 200-mesh material produced by the mill. The efficiency is also expressed in terms of tons of minus 90-mesh material produced by the mills to correspond to the standard practice on the Witwatersrand.

The results given for the performance of the tube mills grinding in closed circuit with cones (Fig. 1) were taken from previous tests carried

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¹ H. A. White: Theory of Tube Milling. *Jnl. Chem. Met. & Min. Soc. of South Africa*, 15 (February, 1915), 190.

² S. E. T. Ewing, C. R. Davis and J. L. Willey: Recent Developments in the Fine Grinding and Treatment of Witwatersrand Ores. *Trans.* (1925) 71, 983.

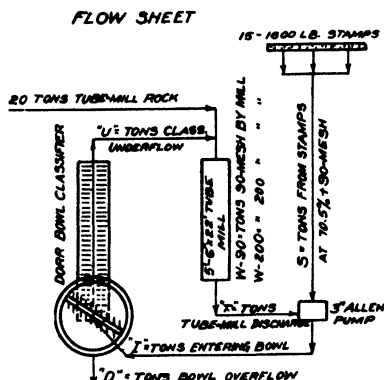


FIG. 3.—FLOW SHEET OF MILL GRINDING IN CLOSED CIRCUIT WITH DORR BOWL CLASSIFIER.

Tube Mill 5 ft. 6 in. by 22 ft.

Classifier, type DSDB, 6 ft. by 23 ft. 4 in. by 8 ft. diameter bowl during test C and 9 ft. diameter bowl during test D. Classifier tank set at slope of 2 in. in 12 in.

	SPEED OF RAKES	TEST C	TEST D
Reciprocating		20.7 s. p. m.	20.7 s. p. m.
Bowl		7.3 r. p. m.	5.5 r. p. m.

Finished product desired.

Test C, 90-mesh separation.

Test D, 150-mesh separation.

CAPACITY OF TUBE MILL IN CLOSED CIRCUIT WITH DORR BOWL CLASSIFIER

[See Sketch Above]	Test C, -90 mesh Separation				Test D, -150 mesh Separation			
	Tons	H ₂ O, Per Cent.	Grading		Tons	H ₂ O, Per Cent.	Grading	
			+90, Per Cent.	-200, Per Cent.			+90, Per Cent.	-200, Per Cent.
Leave stamps <i>S</i>	210.0	73.4	70.5	20.0*	188.0	71.0	70.7	20.0
Leave tube mill <i>T</i>	364.0	28.6	33.9		377.0	28.0	33.0	42.6
Enter bowl <i>I</i>	574.0	59.5	47.3		565.0	59.0	45.6	35.1
Bowl overflow <i>O</i>	230.0	81.0	2.0	78.2	200.0	82.2	1.0	88.7
Classifier underflow <i>U</i>	344.0	18.0	77.5		385.0	19.0	70.0	5.7
90-mesh by mill <i>W</i> -90.....	163.4				143.0			
200-mesh by mill <i>W</i> -200.....	137.9				139.8			
Class. Efficiency <i>E</i> , per cent.....		73.0			64.1 at 90 mesh; 83.1 at 200 mesh			
Circulating load 100 <i>T</i> / <i>O</i> , per cent.....		158.0			182.5			

* Not taken during test C, but same battery screen ($\frac{3}{4}$ in.) as during test D.

Fig. 2 shows the tests with straight type Dorr classifier and Fig. 3 those with the Dorr bowl classifier. Table 1 compares the results from the three types of classification tested.

TABLE 1.—Comparison of Capacity of Tube Mills in Closed Circuit with Cones, Straight-type Dorr Classifiers and Dorr Bowl Classifier

Data Taken From Above Tests at 90-mesh Grinding. Standard Tube Mill 5 Ft. 6 In. by 22 Ft.

	TONS MADE BY MILLS		RELATIVE EFFICIENCY BASED ON 90-MESH PER CENT.	
	90-MESH	200-MESH	90-MESH	200-MESH
Cones.....	140.0	109.5	100	100
Straight classifier.....	160.3*	127.1*	115	116
Bowl classifier.....	163.4	137.9	117	126

* Results obtained from tests A and B; tube mill 6 ft. 6 in. by 20 ft. divided by 1.27 to obtain relative results so as to compare with those obtained from tube mill 5 ft. 6 in. by 22 ft.

At the conclusion of the tests, all factors considered, it was thought conservative to rate the relative efficiency of a tube mill grinding in closed circuit with the various systems of classification, as under Geduld conditions and at 90-mesh grinding, as given below.

	PER CENT.
Cones.....	100
Straight type Dorr classifier.....	117
Bowl type Dorr classifier.....	125

STRAIGHT TYPE DORR CLASSIFIERS AT GEDULD MILL

On completion of the tests discussed, seven Dorr classifiers, straight type, were installed in the new section of the Geduld mill. Available floor space and local conditions unfortunately eliminated the possibility of installing bowl classifiers. The machines installed were 8 ft. wide by 18 ft. 4 in. long, set at a slope of $2\frac{1}{2}$ in. in 12 in. and arranged for driving at three speeds, 18, 21, and 25 s. p. m. respectively. The object of the three speeds was chiefly to provide for coarser grinding should the company desire to mill a greater tonnage. Coarser grinding would result in higher final residues. Since operation started 18 s. p. m. has been found the most satisfactory speed. Change in the grade of overflow, if desired, is made by a control of the moisture within the classifier.

Forty 2,200-lb. stamps.

Old cones used to dewater stamp product. Product from any battery can flow by gravity to any one of three cones.

Seven tube mills, 6 ft. 6 in. by 20 ft. in closed circuit with seven Dorr classifiers, type DSD, 8 ft. by 18 ft. 4 in. Classifiers on floor directly over mills. Classifier underflow can flow by gravity to any one of three tube mills.

Tube mill discharges flow by gravity to central pumping station, elevated and distributed to the seven classifiers, as under old installation with cones.

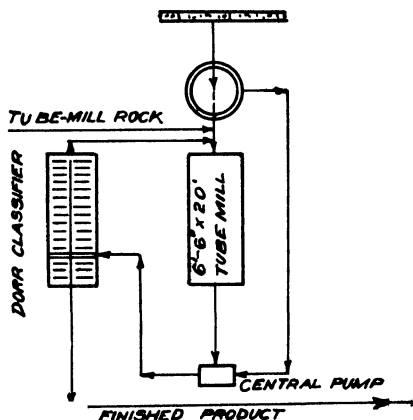


FIG. 4.—FLOW SHEET OF INSTALLATION AT THE GEDULD MILL.

Fig. 4 shows the flow sheet of the Geduld installation. It is not as it might be arranged for a new plant, but has been made to suit the local conditions. The installation, which took advantage of equipment already installed, offers a great flexibility in control and has proved very satisfactory. The underflow from a classifier can feed any one of three tube mills; a classifier going out of service does not "tie-up" a tube mill; nor in turn does a mill out of order necessarily shut down a classifier.

The classifier installation at the Geduld mill was completed during July, 1925. The first full month's operation (August, 1925) showed a net gain from the section of 5,000 tons, and at the same time an improved grading in the finished product of about 2 per cent. in the minus 90-mesh and 4 per cent. in the minus 200-mesh, with corresponding reduction in the final residues. The power to drive the tube mills remained practically constant at 207 hp., average for each of the seven mills.

To compare the August results with those of the best work heretofore obtained under the old conditions, the tonnage of minus 200-mesh material produced by the section was increased 18 per cent., a figure which practically checks that expected as a result of the tests. As the operators become better acquainted with the new conditions, the work of the tube mills should be further improved.

Because of the increased circulating load in the tube mills and the ability to maintain a continuous full feed to the mills under the new conditions, the consumption of tube-mill rock has decreased about 25 per cent. This condition caused considerable trouble at the initial operation of the altered section, as the operators insisted on feeding tube-mill rock as under the old conditions. Enough tube-mill rock has always been hard to get in the Far Eastern section of the Witwatersrand so that a reduction in the quantity required is welcomed.

IMPORTANCE OF QUALITY OF FEED

The work at the Geduld mill demonstrated the importance of "quality" of feed sent to a tube mill as well as "quantity." The importance of quality of feed in tube and ball milling was pointed out by A. L. Blomfield in his discussion of E. W. Davis' paper³ on "Fine Crushing in Ball Mills," but it has been the writer's experience that few mill men have taken advantage of Mr. Blomfield's remarks. If attention were paid to the gradings of the classifier underflows with a few test runs at different speeds of classifier rakes, the capacity of a good proportion of the tube and ball mills in the average plant could be increased.

The 5 ft. 6 in. by 22 ft. tube mill used in conjunction with the bowl classifier was of old design. The end of this mill had no end screen or auxiliary lifting scoops to assist the discharge by raising this material to the discharge trunnion. The maximum amount of ore that could be fed to the mill was at the approximate rate of 450 tons per diem. Owing to the variations in rate of product from the stamps, the safe working average feed could not be maintained much over that sent to this mill during test C (364 tons per 24 hrs.). With a smaller circulating load, the tube mill with the bowl classifier gave better results than the mill in closed circuit with the straight type. The difference was due entirely to quality of feed.

³ E. W. Davis: Fine Crushing in Ball Mills. *Trans.* (1919) 61, 251.

TABLE 2.—*Summary Showing Quality of Feed to Tube Mills during Tests*

Test	Classifier Gradings			
	Underflow		Overflow	
	+90, Per Cent.	—200, Per Cent.	+90, Per Cent.	—200, Per Cent.
A Straight type.....	63.3		2.00	77.7
B Straight type.....	72.6		2.00	73.1
C Bowl type.....	77.5		2.00	78.2
D Bowl type.....	70.0	5.7	1.00	88.7

To illustrate the significance of quality of feed, assume the underflow of the machine in test *C* to be that obtained in test *A*. The feed to classifier and the overflow products were practically the same in both tests. Given the tonnage of overflow and gradings to and from the classifier, the tonnage of the underflow may be found.⁴

Conditions

Grading feed entering bowl <i>i</i>	47.3 per cent. + 90 mesh test <i>C</i>
Grading bowl overflow <i>o</i>	2.0 per cent. + 90 mesh test <i>C</i>
Grading class. underflow (<i>u</i>).....	63.3 per cent. + 90 mesh test <i>A</i>
Tonnage overflow <i>O</i>	230 test <i>C</i>
Tonnage tube mill rock added <i>TR</i>	20 test <i>C</i>
Tonnage classifier underflow <i>U</i> :	

$$U = \frac{I(i - o)}{(u - o)} = \frac{230(47.3 - 2.0)}{63.3 - 47.3} = 651 \text{ tons.}$$

Tonnage fed to tube mill would have been $TR + U = 671$ tons.

The finer feed to the tube mill would have given a discharge from the mill containing a greater percentage of minus 90-mesh material and a corresponding finer feed to the classifier. The finer feed to the classifier, however, would have resulted in a greater percentage of minus 90-mesh material in the classifier underflow.

Had the straight type of classifier been substituted for the bowl and operated as under conditions of test *A*, the tests indicate the following results would have been obtained:

⁴ Standard classification formulae:

$$U = \frac{(i - o)}{(u - i)}; U = \frac{I(i - o)}{(u - o)}; O = \frac{I(u - o)}{(u - i)}$$

Where *I*, *O* and *U* equal the tonnage of input, overflow and underflow, respectively, and *i*, *o* and *u* the fraction (or percentage here) plus material at any given mesh, classifier input, overflow and underflow.

	TONS	GRADINGS OVER 90-MESH, PER CENT.
From stamps.....	195	70.5
Tube-mill rock added.....	20	100.0
Classifier underflow.....	344	60.0
Tube-mill discharge.....	364	20.2
Classifier feed.....	559	37.7
Classifier overflow.....	215	2.0
Classifier efficiency, 57.5 per cent.		
Minus 90-mesh material made by mill.....	153	

A study of tests *A* and *B* will show the relative importance of quality of tube-mill feed. During the second test, the tonnage of minus 90-mesh material produced was greater with a decrease in circulating tonnage within the mill amounting to 234 tons per diem. The 6 ft. 6 in. by 20 ft. tube mill was of recent design, equipped with end screen and auxiliary lifting scoops at the discharge end. The mill apparently handled a feed of 1,000 tons per diem satisfactorily. Had it not been for the failure of our pump to handle a higher circulating load during test *B*, there is little question but that the efficiency of the mill could have been increased during this test by maintaining the first tonnage of feed to the mill.

CLASSIFIER SPEED

The possibilities of increasing classifier and tube-mill efficiencies by changing the speed of rakes on a classifier has been mentioned in a previous paragraph. The proper speed for any classifier at a given plant can only be determined by trial. For average conditions, definite speeds have been recommended for given mesh separations, but certain local conditions such as character of pulp, moisture in overflow and tonnage handled in a given classifier often call for a change. A quick-settling ore pulp such as that found on the Witwatersrand where a pulp contains practically no real "slime," requires a higher speed of classifier rakes for a given mesh separation than the viscous "slimy" pulps generally found in the cyanide plants throughout Mexico. The tendency in recent years has been to increase the speed of bowl rakes considerably over that recommended in some of the earlier installations. Speeds of 4, 6, 8 and even higher r. p. m., depending on diameter of bowls and separation desired, are not uncommon.

Table 3 shows the results obtained by changing speed of classifiers at Springs Mines, Ltd., Transvaal, South Africa. Two type DSDB bowl classifiers were used with tanks 6 ft. wide by 26 ft. 8 in. long by 16 ft. diameter. The classifiers made a "sand-slime" separation for sand leaching and slime treatment. A "slime" was desired containing about 88 to 90 per cent. minus 200-mesh material and a "sand" with a minimum amount of minus 200-mesh product.

TABLE 3.—*Results from Changing Speed of Classifiers*

	Daily Tonnage Each Classifier		Gradings, Accumulative Per Cent.			
	Tons	Percent- age	+60	+90	+200	-200
Period A						
Reciprocating rakes 12 s. p. m.						
Bowl rakes 1.6 r. p. m.						
Enter bowl.....	800	100.00	0.26	10.68	38.10	61.9
Bowl overflow (slimes).....	454	56.70		0.70	8.60	91.4
Classifier underflow (sands)...	346	43.30	0.50	19.40	76.80	23.2
Period B						
Reciprocating rakes 17 s. p. m.						
Bowl rakes 4 r. p. m.						
Enter bowl.....	679.2	100.00	0.26	11.40	37.12	62.88
Bowl overflow (slimes).....	461.7	68.00		0.60	12.40	87.60
Classifier underflow (sands)...	217.5	32.00	0.80	34.30	89.60	10.40 ^a

^a Practically all sulfides.

PRACTICE IN THE WITWATERSRAND

The ore from the Witwatersrand, apart from that in the Far East section, yields a satisfactory recovery by means of "corduroy" tables and cyanidation when crushed to grade about 5 to 10 per cent. plus 60 mesh with a corresponding total of 75 to 80 per cent. minus 90 mesh. To obtain this comparatively coarse product, Caldecott cones are used exclusively for the classification in closed circuit with tube mills. By the use of one or more so-called "safety" cones, following the primary cone at the head of the tube mill, a good feed is obtained for the latter. The quality of feed to the tube mills, in plants working throughout this older section of the reef, is reflected in a unit production of minus 90-mesh material for a "standard" tube mill 5 ft. 6 in. by 22 ft., amounting sometimes to more than 160 tons. (City Deep, Ltd.)

A substitution of mechanical classifiers for cones, throughout the older sections of the reef where comparatively coarse grinding is done, would undoubtedly increase the grinding efficiency of the tube mills. The amount of this increase in efficiency for their conditions could only be determined by trial. The mechanical classifiers should give a better feed to the tube mills than that now obtained by use of cones, and at the same time allow for a greater circulating load within the mills without loss of classification efficiency. The failure of a cone to handle a high circulating load without loss in classification efficiency is one of its limiting features. Savings in pumping charges alone would go a long way towards paying for a change from cones to mechanical classifiers.

With the exception of several mills in the Far East, "sands" and "slimes" are treated separately by cyanidation throughout the Witwatersrand. The practice has been to separate the sands and slimes by the use of cones usually assisted by a further recovery of slimes from the sand collectors. The sands after draining, are transferred to treatment tanks. (New Modderfontein also Simmer & Jack collect and treat sands in same tanks.)

BOWL CLASSIFIERS AT THE SPRINGS MINES MILL

In the summer of 1925, two Dorr bowl classifiers were installed in the old section of the mill of Springs Mines, Ltd. (new section is "all sliming") to make a "sands-slimes" separation. The classifier underflow is sluiced direct to sand-treatment tanks with cyanide solution, the bowl overflow goes by gravity to the slime collectors. Sand collectors, with corresponding sand transfer, are eliminated. Table 4 gives a summary of the results obtained.

TABLE 4.—*Summary of Classification, Sand-slime Separation*

	GRADINGS,	ACCUMULATIVE,		PER
	+60	+90	+200	CENT.
				—200
Cone classification, Jan.—June, incl., 1925				
Enter cones.....	0.30	7.60	33.90	66.10
Sands (sent to treatment tanks).....	1.10	20.90	81.50	18.50
Slimes.....		0.40	9.20	90.80
Dorr bowl classification, average Aug. and Sept., 1925				
Enter bowls.....	0.26	10.68	38.10	61.90 ^a
Classifier underflow (sands).....	0.80	31.60	89.50	10.50
Bowl overflow (slimes).....		0.50	13.10	86.90

^a Calculated.

Size, type and average tonnages handled by these classifiers have been previously mentioned.

The tendency of all types of classifiers, in closed-circuit grinding, to retain the coarse gold and heavy sulfides within the circuit until they are ground extremely fine has been known for years. The extent to which the gold was accumulated within circuit of the bowl classifier and tube mill is shown by the analysis of a sample taken during test *D* at the Geduld mill.

CLASSIFIER UNDERFLOW, TEST *D*

GRADING		PER CENT. TOTAL	ASSAY VALUE, DWTS.
	+ 90	72.00	8.75
- 90	+200	22.80	23.75
-200		5.20	69.50
		100.00	15.32 (Calculated)

Value of original ore from stamps, approximately 7.00 dwts. Approximately 42 per cent. of the product in the classifier underflow came direct from the stamps (See Fig. 3).

POSSIBLE USE OF BOWL CLASSIFIERS

The possibilities of using the bowl type of classifier as a concentrator are being seriously considered on the Witwatersrand. The proposal is to pass 1,000 to 2,000 tons through a single bowl classifier, depending on size of units used, and to remove as an underflow approximately 10 per cent. of the original tonnage. The value per ton of the classifier underflow undoubtedly would be several times that of the original. A special independent grinding unit to insure the grinding of this small portion of ore to an extremely fine state should give a better average final residue.

A change from single- to multiple-stage grinding at the McIntyre mill, Canada, without increase in number of grinding units carries out very much the same idea as that suggested for the Witwatersrand. Bowl classifiers are used in the second stage at the McIntyre mill, and it is understood that their final residues have been lowered considerably.

ACKNOWLEDGMENT

The writer is indebted to Messrs. White and Willey for the data given covering the classification work done at Geduld and Springs.

DISCUSSION

G. H. CLEVENGER, Boston, Mass.—Fortunately with proper classification the required degree of concentration can be obtained, but sometimes the part of the ore requiring finest grinding does not always get it. In grinding for the cyanide process, it is usually desirable to grind the heavy or concentrate part of the ore as fine as possible without wasting energy in unnecessary grinding of the gangue. This situation is met, to a certain degree, by the cone or mechanical classifier. In grinding for concentration, the gangue should be ground to whatever degree is necessary to free the mineral, but once the mineral is freed it should be broken as little as possible. Strict observance of this rule is less necessary perhaps with flotation but it is still rather important. Only by stage grinding and successive classification can this condition be approximated.

C. P. McCORMACK, Cleveland, O.—If the gangue is of material that tends to ball up the classifier, how would you handle that condition?

B. R. BATES.—I do not know as I have ever met that in ordinary gold and silver work; I have never been troubled with any accumulation and balling up on the balls, although it does take place in clay washing.

G. H. CLEVINGER.—Is this a case where the clay balls are not broken up or one where they are but there is so much clay that part passes over with the coarse part of the ore?

C. P. McCORMACK.—It is a divided condition between the action of the links; it becomes balled in the classifier, then gums up the tube mill.

B. R. BATES.—I admit that I have never run into that in any metallurgical work.

G. H. CLEVINGER.—In general, with ores that are finely ground, the clay is broken up and has little tendency to come together to form masses that might cause difficulty in classification. Clay balls, when no provision is made to break them up, have at times caused gold losses in dredging operations.

C. P. McCORMACK.—I notice it especially in the manganese ores of South Russia where they are washed.

G. H. CLEVINGER.—That is washing ore rather than grinding, is it not?

C. P. McCORMACK.—It is held in the classifier without any preliminary grinding.

G. H. CLEVINGER.—The only remedy for such a condition is to provide means to break up and distintegrate the clay masses so that the washer or classifier can effectively remove them.

B. R. BATES.—All types of classifiers in general use in metallurgical plants tend to retain the heavier material in the grinding circuit. No tests were made at Geduld to determine the relative merits of the various classifiers to retain the heavier material in the closed grinding circuit.

The importance in retaining the heavier part of the ore in the grinding circuit is brought out in a paper by Messrs. Wartenweiler and Graham, *Bulletin* of the Institution of Mining and Metallurgy, 1924, No. 239. The authors determined that on the Witwatersrand it was necessary to grind all the gold to—260 mesh so that it might be dissolved in a short agitation of about 8 hours.

C. E. LOCKE, Cambridge, Mass.—Have their investigations given any definite ratio between the quartz gangue, the pyrite and the gold ore?

B. R. BATES.—We did not attempt to make such tests. That has been carried on extensively in connection with the work on hydraulic classifiers. Taking into consideration the agitation going on in the classifier and the specific gravity of the pulp used, I can see no reason

why the law determined under hydraulic conditions would not be the same.

J. A. BAKER, Newfield, N. J.—Perhaps the question raised by Prof. Taggart would be answered by the results obtained at McIntyre. By using two closed sections, they have built up the concentrated pyrite in the subsequent ore to 15 per cent., whereas the pyrite in the original ore is from 3 to 4 per cent.

A. F. TAGGART, New York, N. Y.—How much finer is the pyrite and what is its maximum size?

J. A. BAKER.—It is substantially finer than the quartz.

A. M. GAUDIN, New York, N. Y.—I noticed in Mr. Bates paper that in one instance the efficiency is given as 64 per cent. at 90 mesh and 83 per cent. at 200 mesh. It has been our experience at Columbia that classifier efficiencies are not the same when rated on different sizes as a basis. In fact, they do not always turn out to be positive efficiencies. Should not such efficiency have the same value no matter what size was used as a basis?

B. R. BATES.—That point was merely in using the formula as stated; if you were working for 200 mesh, you could figure the efficiency on that basis; or if you were trying to get 90-mesh material, the efficiency should be based on 90-mesh separation.

A. M. GAUDIN.—Should it not be the same?

B. R. BATES.—No. If you were trying to get 200-mesh material and had certain results, your efficiency would be a certain sum, based upon your ability to produce 200-mesh material; but if you were working for a 90-mesh material, the efficiency would be based upon the amount of 90-mesh material resulting, plus or minus.

A. B. PARSONS, New York, N. Y.—The difference between the scientific and the commercial mind, perhaps.

B. R. BATES.—No. The point is that if you are aiming for a 200-mesh overflow, 80 per cent. efficiency would be one figure. But if you were trying to get 100-mesh material, then the result based on 100 mesh would be different from that on 200 mesh. If you were trying to get 200-mesh overflow and you had 100 per cent. —200 in the overflow and no —200 in the sand return, you would have 100 per cent. efficiency. But if you were trying to get 100-mesh overflow and got 100 per cent. —200 mesh in the overflow, you would be doing a poor job; it certainly would not be 100 per cent. efficiency at 90-mesh separation.

A. M. GAUDIN.—It was my impression that the efficiency of a certain classifier operation should be the same no matter on what screen the computation of efficiency is based.

B. R. BATES.—If you were trying to get 100-mesh overflow and you got all 200-mesh overflow and no —200 mesh in your sands, it would be 100 per cent. efficient at 200 mesh but would not necessarily be 100 per cent. efficient at 100 mesh.

The formula for classification efficiency, mentioned here, has been used in the Southwestern copper district.

An Investigation of Crushing Phenomena

BY A. M. GAUDIN,* NEW YORK, N. Y.

(New York Meeting, February, 1926)

THE study that is presented here was undertaken in order to condense information concerning comminution, and covering a great variety of conditions, into one or several rules which would be of use in the development of a systematic theory as well as in many directly practical ways. As the result of this work, the following conclusions appear justified:

1. Rocks may be classified, from the point of view of comminution, into two general classes which are (a) structurally homogeneous, and (b) structurally heterogeneous. Structurally homogeneous rocks are those in which fracture takes place through grains and grain boundaries alike; heterogeneous rocks are those in which fracture passes in preference through grain boundaries.

2. If a sized product composed of structurally homogeneous rock grains is crushed, a product results in which the relation between the percentage weight of grains of various sizes and these sizes themselves follows a definite law. This is not true of structurally heterogeneous rocks.

3. Ball milling with structurally homogeneous rocks, and under certain conditions, presents exceptions to this rule.

4. In ball milling with structurally homogeneous rocks, there exists a critical ratio of size of feed to size of balls, above which the machine operates essentially by surface wear, and below which it operates essentially by breaking across the body of the particle.

5. In ball milling, with structurally homogeneous rocks, and when the size of feed grains exceeds the critical size, the particles worn off are of a substantially definite size which depends upon the ball size.

6. In the case of a typical heterogeneous rock, such as Manhattan schist, particles are crushed in such a way that there is a greater proportion of grains of the size that is the average grain-size of the rock than there would be in that range of size with a structurally homogeneous rock. This has been found to be true with all the crushers tested.

7. Different methods of crushing produce grains of different shapes.

8. The importance of sizing the -200-mesh portion of a crushed product, in crushing-efficiency investigations, has been greatly under-

* Lecturer in Mining, Columbia University.

estimated.¹ Without accurate information concerning material of that range of size, the usefulness of efficiency computations is doubtful.

Homogeneous vs. Heterogeneous Rocks

Rocks are of different degrees of induration; some are cemented so substantially that fracture will take place with equal ease through mineral grains or cement; others are so loosely compacted that they crumble under slight pressure. The fracture of rocks in which grains are interlocking and in which there is little or no cementing of grains, such as vein-quartz, is directly across the grains with no respect to grain boundaries. The fracture of rocks having weakly bonded grains, such as Manhattan schist, goes around the grains, following the grain boundaries. It appears possible, on this basis, to classify rocks into two general classes: The structurally homogeneous and the structurally heterogeneous. Typical examples of these classes, in one case at least, are granite for the homogeneous rocks; schist, sandstone or weathered crystalline limestone for the heterogeneous rocks. It is fair to assume that all gradations exist between typical examples of these classes of rocks. This assumption is confirmed by the experiments with Manhattan schist.

The various crushers tested were the following: Dodge jaw crusher, 4 by 7 in.; "Krom" rolls, 10 by 16 in.; batch ball-mill, 8 by 10 in. (rotating cylinder); batch rod-mill (same cylinder filled with rods instead of balls); and 20-in. continuous-discharge Hardinge ball mill. Especial stress was laid on testing the rolls, batch ball-mill and batch rod-mill on account of the great flexibility of these machines.

In investigating a crushed product, to know the shape of the particle is useful for qualitative reasoning but size alone furnishes quantitative estimation. A complete account of the procedure used in sizing the products of the various crushers is given in another paper,² which details the manipulation, computation and interpretation of sizing tests as they were carried out in the present investigation.

The size curve of a broken product is a graphical representation of the sizing test made on that product. It will, of course, depend on the material used in the test, the crusher, and the size-curve of the feed to the crusher. In order to minimize the number of variables entering, closely sized products were fed.

¹ A. O. Gates: Crushing-surface Diagram. *Eng. & Min. Jnl.* (1913) **95**, 1039; Diagram of Crushing Efficiency. *A. I. M. E. Trans.* (1917) **55**, 685; also Kick vs. Rittinger: An Experimental Investigation in Rock Crushing Performed at Purdue University. *Trans.* (1916) **52**, 875.

² A. M. Gaudin: Sizing Analyses and Their Interpretation. In manuscript.

In representing graphically the sizing tests of broken products, two plots have been used: The semilogarithmic plot in which the percentage of material retained by a screen and passing the next larger screen (in a Tyler standard series) is plotted against the logarithm of the screen aperture; and the logarithmic plot in which the logarithm of the percentage of material retained is plotted against the logarithm of the screen aperture. A convenient base for screen-aperture logarithms is the screen-aperture ratio, and a convenient base for the percentage logarithms is 10. It is thus seen that the scales used for the aperture and percentage coordinates in the logarithmic plot are not the same unless the paper is ruled so as to make them identical.

The first difficulty encountered in an investigation of comminution is that a sizing operation is generally associated with a breaking operation, so that the results observed involve both. For instance, a positive sizing action is exerted by the jaws of a crusher or the concaves and head of a gyratory, even if the maximum size of particle that goes through the crusher varies with the position of the crushing parts. A positive sizing action is exerted as well in a Braun disk pulverizer, a Symons disk crusher or crushing rolls. In stamp-mills there are three sizing actions: First, a nonpositive sizing action as the stamp comes down on the shoe, since large grains of rock will protect small grains from being crushed as long as they themselves are not reduced to a smaller size; secondly, the nonpositive sizing action of the water; thirdly, the positive sizing action of the discharge screens. In rod mills, large pieces protect small pieces by keeping the rods apart. This is nonpositive sizing, but, curiously enough, appears as efficient as many positive sizing actions. In ordinary dry ball or pebble mills, there is no true sizing action, but other elements enter to complicate the problem.

HOMOGENEOUS ROCKS

CRUSHING ROLLS

The typical size-curve (semilogarithmic plot), obtained with crushing rolls fed with quartz coarser than the set of the rolls, is shown in Fig. 1. It is characterized by a maximum M and two inflection points T_1 and T_2 . The corresponding semilogarithmic cumulative plot (Fig. 2) is well known. Neither of these curves is geometrically simple. On the other hand, the logarithmic plot is a straight line in the fine range, and a paraboloid loop in the coarse range (Fig. 3). Figs. 4 to 10 record the results of a number of tests. Within the range of the straight line BC , the relation between the percentage of material y , and screen aperture x , is, of course:

$$\log y = k \log x + \log C \text{ or} \quad (1)$$

$$(2)$$

where C is a constant and k the slope of line BC . It appears immediately that the value of k is of prime importance. For instance, material having

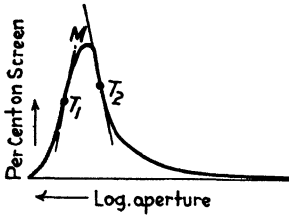


FIG. 1.

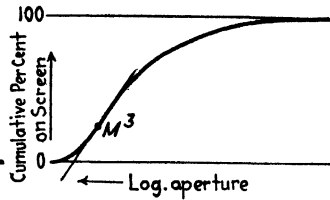


FIG. 2.

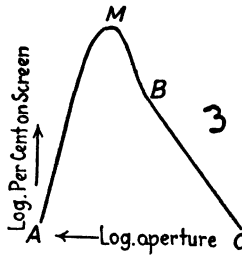


FIG. 3.—SIZE-CURVES OF ROLL PRODUCTS.

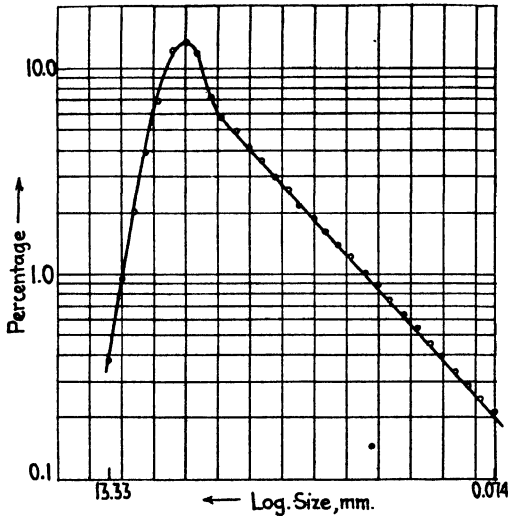


FIG. 4.—FEED, QUARTZ THROUGH 18.85 MM. AND ON 13.33 MM., ONE-STEP CRUSHING TO 5.613 MM. IN CRUSHING ROLLS.

a large value for k , that is a steep BC line, will contain less fines than a material having a flat BC or small value for k .

The results of several tests indicate that for a certain set of the rolls, k decreases with increase in the ratio of size of feed to set of rolls, that is,

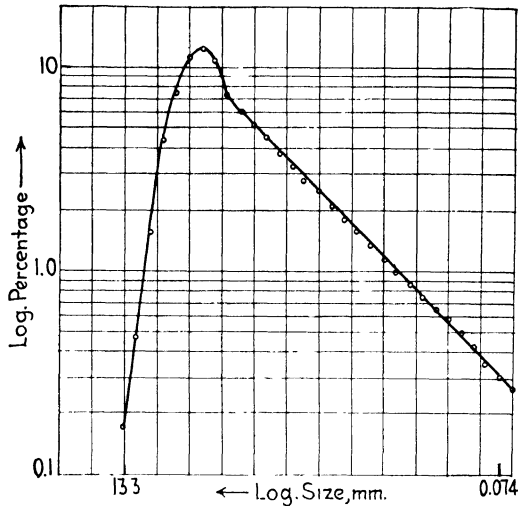


FIG. 5.—FEED, QUARTZ THROUGH $1\frac{1}{2}$ IN. AND ON 26.6 MM. CRUSHED IN ROLLS SET AT 5.613 MM.

when a large reduction-ratio is adopted, more fine material results (Fig. 11). This is in line with the accepted contention that “stage crushing”

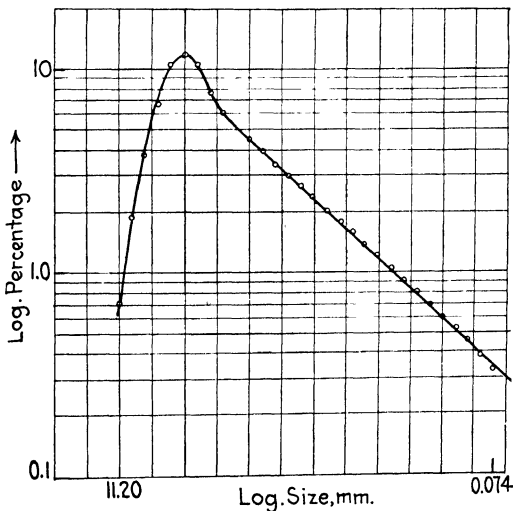


FIG. 6.—FEED, QUARTZ THROUGH 2 IN. AND ON $1\frac{1}{2}$ IN., CRUSHED IN ROLLS SET AT 5.613 MM.

makes less fine material than crushing that involves a large reduction in size in one stage. To obtain further information in this line, two tests

were performed (Figs. 4 and 10) on quartz + 13.3 – 18.8 mm., the rock being crushed with the rolls set at 5.6 mm. in one case and at 13.3, then

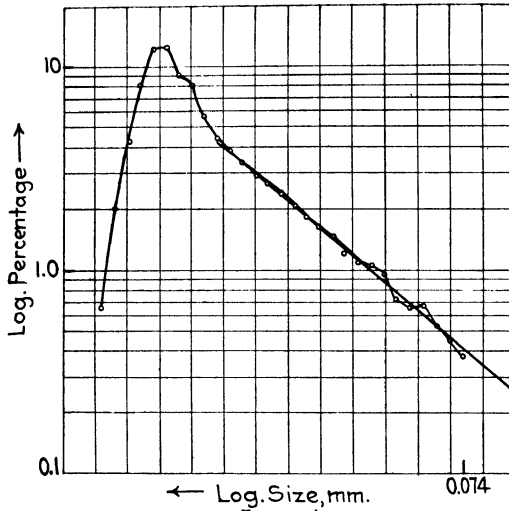


FIG. 7.—FEED, STONY CREEK GRANITE, THROUGH 22.43 MM. AND ON 18.85 MM., CRUSHED IN ROLLS SET AT 5.613 MM.

11.20, 9.33, 7.92, 6.68 and 5.61 mm. in the other case. The percentages of –100-mesh material obtained were 1.76 and 1.36 respectively—which

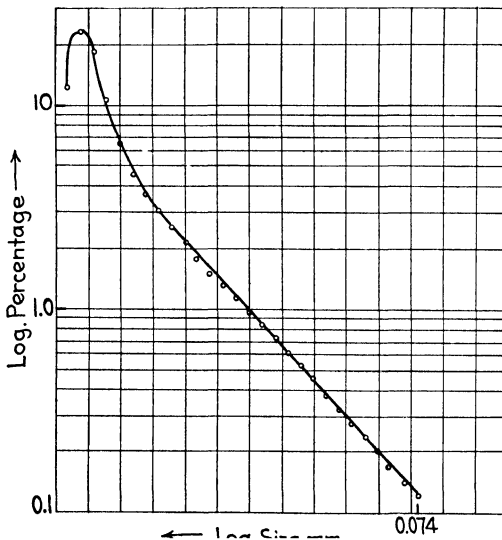


FIG. 8.—FEED, GALENA THROUGH 9.423 MM. AND ON 6.680 MM., CRUSHED IN ROLLS SET AT 5.613 MM.

seemingly supports the contention that stage crushing produces less fine material.

In crushing quartz, a feed made up of flat grains gives a smaller value for k than one made up of roughly equidimensional grains. Using, as

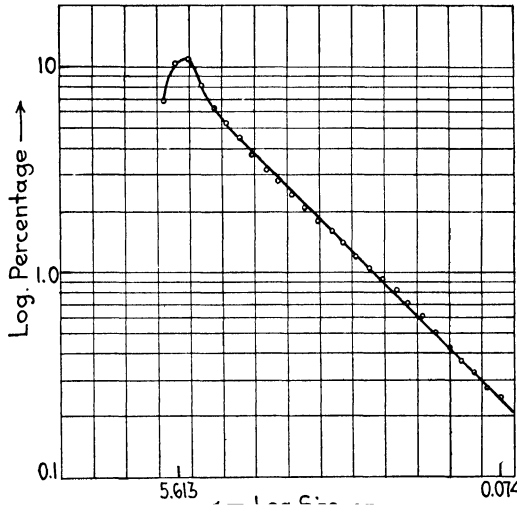


FIG. 9.—FEED, GALENA THROUGH 13.3 MM. AND ON 9.423 MM., CRUSHED IN ROLLS SET AT 5.613 MM.

feed, grains that stay on an 18.85-mm. Tyler screen and pass through a 22.43-mm. screen, but had smallest dimension of 5 to 14 mm. and 18 to

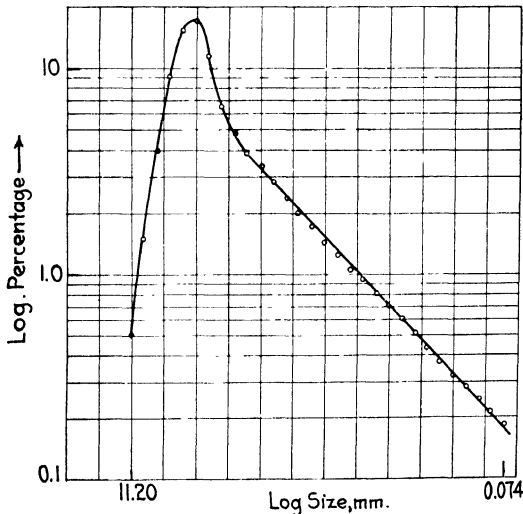


FIG. 10.—FEED, QUARTZ THROUGH 18.85 MM. AND ON 13.33 MM. CRUSHED IN STEPS IN ROLLS SET AT 5.613 MM.

23 mm. respectively, the values of k were 0.82 and 0.90, respectively—a material difference.

The most striking fact disclosed by these tests, however, is the great variations in k for materials of different characteristics under otherwise similar conditions. Fig. 11 indicates, in spite of the paucity of data concerning galena, that the softer galena yields much more fine material than the harder quartz under similar reduction-ratios.

The shape of grains made by crushing quartz in rolls varies with the size of the grains (see Figs. 12, 13, 14, 15, 16, 17); the coarsest grains—those that would stay on a screen having an aperture greater than the set of the rolls—are distinctly flat; the middle-range grains, which correspond to sizes presenting the greatest frequency (apex of curved section in logarithmic plot) are of a more or less equidimensional character, roughly tetrahedral fragments being common. The fine-range grains (corresponding to the straight-line portion in the logarithmic plot) are generally

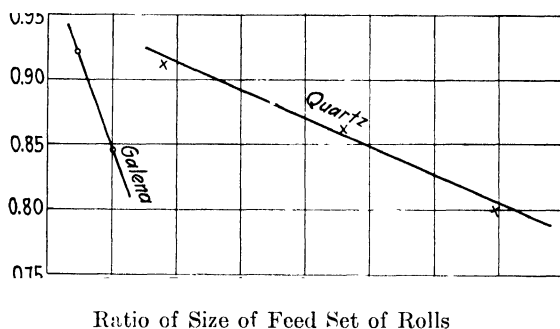


FIG. 11.— K vs. $\frac{\text{SIZE OF FEED}}{\text{SET OF ROLLS}}$; SET OF ROLLS IS 5.613 MM.

rather elongate with acicular forms frequent. The difference in shape between the grains of the coarse range and the middle range can be ascribed to the combination of the sorting actions of the screens and the rolls, which are different: Rolls size in the same fashion as a grizzly and the determining particle dimension is the minimum dimension; square-mesh testing sieves sort, primarily, on the intermediate dimension of the particle, hence the testing sieves make a further size distinction imposed upon that made by the rolls. This results in placing in the coarsest testing-sieve sizes the large, flat particles and in the intermediate sizes the particles of the same thickness but of lesser width. A combination of similar sorting actions cannot, however, explain the difference in shape between the middle-range grains and the fine-range grains, because of the much greater range in size involved. Concurrently a difference appears in the size-curve, indicating the possibility that a different crushing action controls the formation of the coarse and of the fine grains.

Professor Haultain's slow-motion moving pictures indicate that cubical blocks break in rolls in two ways: Firstly, by transversal cracks through the blocks going from roll to roll and yielding more or less

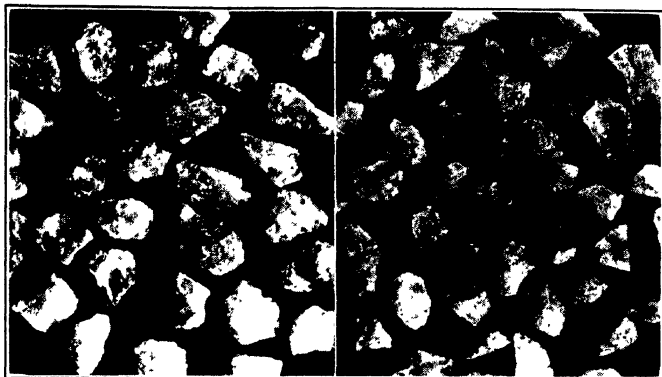


FIG. 12.—On 9.423 mm.

FIG. 13.—On 4.699 mm.

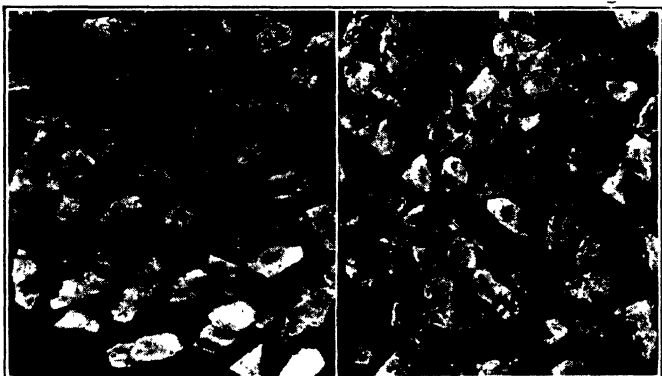


FIG. 14.—On 2.362 mm.

FIG. 15.—On 1.168 mm.

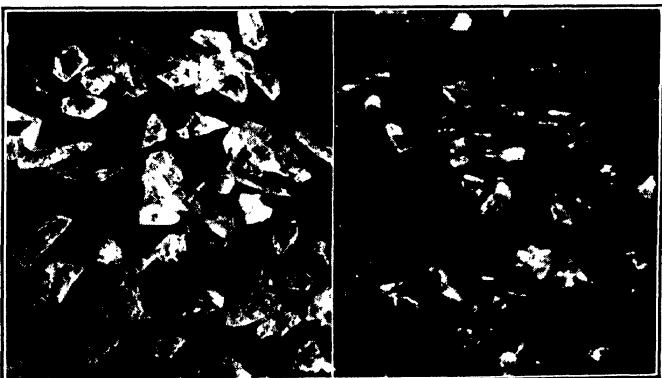


FIG. 16.—On 0.295 mm.

FIG. 17.—On 0.074 mm.

ROLL-CRUSHING PRODUCTS (QUARTZ).

tabular slabs; secondly, by radiating cracks from contact points at the roll faces, the two processes appearing as indicated in Fig. 18. Transverse cracks appear first and the radiating cracks later. From observation of the pictures, proportions of grains made by the two crushing actions appeared to be of the order of 80 and 20 per cent., respectively. This corresponds fairly well with the proportions of grains that

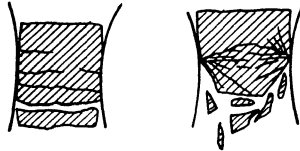


FIG. 18.—SKETCH SHOWING HOW CUBES OF HOMOGENEOUS MATERIAL BREAK WHEN CRUSHED IN ROLLS.

follow, respectively, the paraboloid and straight-line portions of the logarithmic plots of roll-product screen analyses. Assuming that the order of appearance of transverse and radiating cracks is independent of the reduction ratio, then the smaller the reduction ratio, the greater the percentage of breaking that is done by the method of transverse cracks,

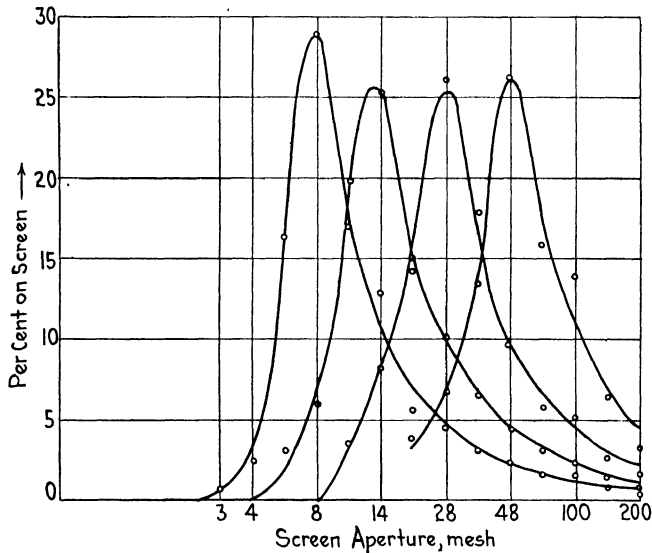


FIG. 19.—TAKEN FROM PROF. HAULTAIN'S DATA: ENGINEERING RESEARCH BULLETIN, No. 4. UNIV. OF TORONTO, P. 155.

and, therefore, the smaller the proportion of fine material that should be expected. This accords with the conclusion that stepped crushing produces a minimum amount of fine material.

The shape of the curved portion of the size-curve is, in a certain measure, dependent on the pressure exerted by the roll springs; it is customary to look upon the set of crushing rolls as being a fixed quantity,

but watching idle rolls to which a fairly large piece of hard material is fed will convince that there is considerable "give" on the part of the springs, with ordinary spring tension. With rolls set close, any "give" is infinitely large compared to the set. Mathematical reasoning is, therefore, that decreasing the size of feed and the set of rolls will mean a proportionately larger "give" on the part of the rolls, hence greater variation in the dimension of the largest piece that can go through the rolls. Accordingly, with finer feed one should expect the curved portion of the logarithmic plot of the screen analysis to be flatter than with coarse feed. Another factor that tends toward the same result is the presence of irregularities in the roll faces. That facts are as described is shown by Fig. 19 which is drawn from Professor Haultain's data, plotted on Fig. 20 with lines of best fit.

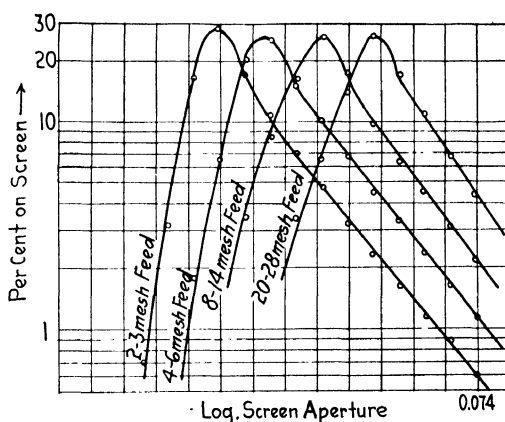


FIG. 20.—PROF. HAULTAIN'S DATA, REDRAWN FROM FIG. 19.

The conclusion that rolls crush by breaking through the particle, as contrasted with surface wear, is supported by Professor Haultain's moving pictures, as well as by the shape of roll-product grains, which by their angularity make surface wear a highly improbable source of manufacture.

JAW CRUSHER

The logarithmic plots of the screen analyses of jaw-crusher products on homogeneous feed are similar to the plots for crushing rolls, in that they present a curved-line and a straight-line portion. Fig. 21 shows the results obtained with a Dodge breaker on Stony Creek granite. The similarity in the plot of the screen analysis of the product of this crusher and the corresponding plot for roll-crushing justifies the conclusion that the action of a jaw crusher is substantially the same as that of crushing rolls.

There are, however, some differences in the performance of these crushers, as indicated by the variation in the steepness of the straight-line portion and the curvature of the curved section of the logarithmic plots of the screen analyses of the products. The Dodge product has a very sharply closed curved section, indicating that the sizing action of the jaws is very efficient. One would naturally expect such a result from a crusher in which the sizing action is positive and does not depend on the resilience of a spring.

The shape of the grains produced is very much like that of the grains produced by rolls. With Stony Creek granite as feed, the jaw crusher appears to make more fine material than crushing rolls, that is the value of k obtained in the case of the jaw crusher is less ($k = 0.61$ vs. $k = 0.71$).

Notwithstanding the fact that, with corrugated jaws, part of the product is broken by beam action, most of the product fed to the crusher

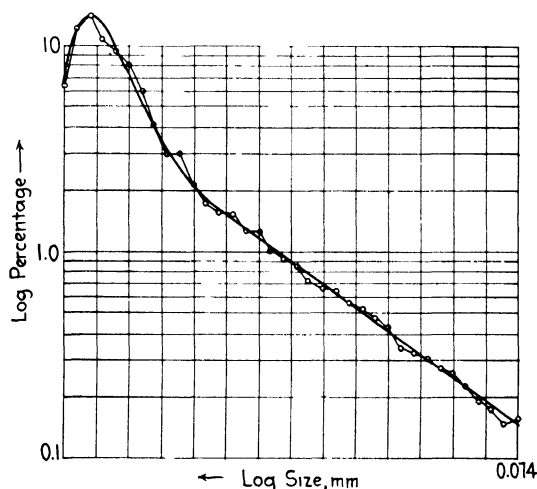


FIG. 21.—FEED, STONY CREEK GRANITE ON 3 IN. AND THROUGH 6 IN., CRUSHED IN DODGE JAW CRUSHER.

is not of such size as to allow breaking by beam action. Furthermore, with plain jaws or with worn, corrugated jaws, the crushing load is slowly applied and the particles take it in short column. This is the same as in rolls and, therefore, the initial transverse breaks and later radiating breaks are similarly to be expected with the resulting similarity in size and shape of crushed product. Accordingly, jaw crushers are to be classified with rolls as devices that crush by breaking through the particle.

GRINDING IN PEBBLE MILL WITHOUT PEBBLES OR BALLS³

The ground products of jaw crusher and rolls were found to be distinctly angular.

³ This work was done jointly with R. T. Bergman, Joplin, Mo.

In nature, both rounded and angular grains are found; rounded pebbles are common in streams, under conditions which indicate that they have traveled and worn for a comparatively short time only; on the other hand, rounded sand grains are rare, even when eons of time, apparently, have been allowed for wearing the grains to a subspherical shape. An unpublished investigation⁴ conducted by Dr. J. J. Galloway, Assistant Professor of Paleontology, Columbia University, discloses the fact that grains of various minerals of the sizes generally referred to, as coarse sand (10 to 30 mesh), become more or less rounded when artificially allowed to wear. The apparatus used by Dr. Galloway consisted of a bottle rotating on its axis, in which a stationary baffle-plate impinged on the grains of sand maintained in suspension in water by the turbulent fluid motion. The duration of these tests was from a few hours to several hundred hours at a speed such that the rate of travel of the grains was about that of sand grains in streams or at beaches; namely, about two miles an hour. Dr. Galloway found that soft minerals wear down very rapidly. Such are the micas, pyroxene, hornblende, and to a lesser extent, the feldspars. Quartz requires perhaps 100 times as long as mica to wear to the same stage of roundness. This would explain the existence of large quantities of quartz sand, and the almost total absence of sands of the softer minerals, in spite of the abundance of these minerals in rocks. Dr. Galloway further finds that:

1. Finer grains are more difficult to wear than coarse grains.
2. Fine product-grains are less rounded than coarse product-grains obtained simultaneously.

A series of tests was made with 1000-gm. lots of quartz grains rotated in porcelain Abbé mills and allowed to wear each other, in order to verify whether Dr. Galloway's conclusions hold true in ball-milling. The size of feed and duration of run were made to vary. With a feed made up of angular quartz pebbles (roll product) passing a 22.43-mm. sieve and retained by an 18.85-mm. sieve, run for 6 days at 51 r. p. m., the product obtained consisted of approximately 88 per cent. round pebbles and gravel, no sand and 12 per cent. of slime, all finer than 10 microns (1 micron = $\frac{1}{1000}$ millimeter). Screen analysis is given in Table 1. With a feed made up of $-7.925 + 6.680$ -mm. quartz, that is, one having roughly one-third the diameter of the feed employed in the previously described test, 1.5 per cent. of material finer than 10 microns was formed. This is only one-eighth of the amount formed in the other test. With a feed made up of $+2.362 - 2.794$ -mm. material, that is one having a little over one-third the diameter of the preceding, the amount of slime under 10 microns in diameter is 0.25 per cent.; that is about one-sixth as much as in the intermediate-feed test and $\frac{1}{48}$ as much as in the coarse-feed test.

⁴ Private communication.

TABLE 1.—*Screen Analysis of Quartz Grains Rotated in Porcelain Abbé Mills and Allowed to Wear Each Other*

Feed 1000 Grams -22.43 + 18.85-mm. Quartz, Run for 6 Days Without Balls

SIZE, MM.	ANALYSIS, PER CENT.	SIZE, MM.	ANALYSIS, PER CENT.
+18.85	58.2	0.417	0.0069
15.65	21.9	.208	.0059
13.33	4.28	.104	.0069
9.423	2.64	.074	.0030
6.680	.35	.037	.045
.699	.238	.0185	.058
.327	.066	.0092	.098
.651	.014	— .0092	12.0
.833	.011		

As the amount of slime produced decreases, so does the roundness of the coarser portions; the coarser grains in the run made with the 2.3–2.7-mm. feed show almost no rounding, while those of the run made with 18.8–

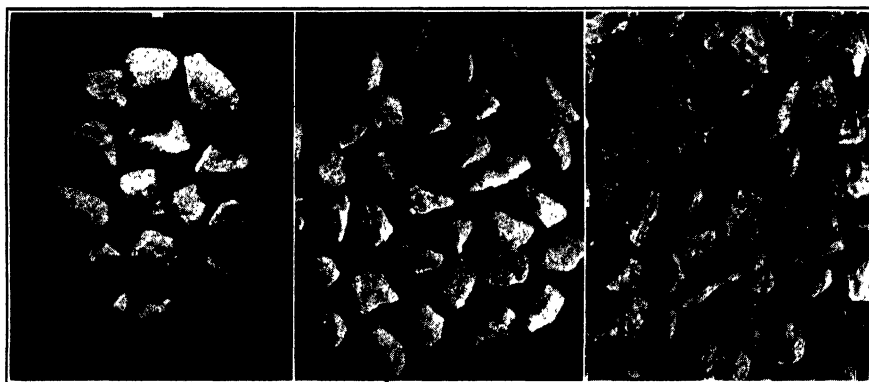


FIG. 22.

FIG. 23.

FIG. 24.

FIG. 22.—QUARTZ ON 18.85 MM. COARSEST GRADE OF MATERIAL OBTAINED FROM FEED ON 18.85 AND THROUGH 22.43 MM. RUN FOR 6 DAYS. WEAR-TESTS PRODUCTS.

FIG. 23.—QUARTZ ON 6.680 MM. COARSEST GRADE OF MATERIAL OBTAINED FROM FEED ON 6.680 AND THROUGH 7.925 MM. RUN FOR 6 DAYS. WEAR-TESTS PRODUCTS.

FIG. 24.—QUARTZ ON 2.362 MM. COARSEST GRADE OF MATERIAL OBTAINED FROM FEED ON 2.362 AND THROUGH 2.794 MM. RUN FOR 6 DAYS. WEAR-TESTS PRODUCTS.

22.43 mm. feed show very considerable rounding (see Figs. 22, 23, 24). It will be observed that the amount of material worn from the grains varies substantially as the square of the diameter of the grains. From these observations the following conclusions appear justified, at least as far as quartz and other minerals that do not exhibit marked cleavage are concerned:

1. Tumbling of grains produces rounding.

2. Wear due to tumbling of grains decreases rapidly with decrease in grain size, other things being equal.

3. The amount of material ground off grains by wear varies substantially as the square of the grain diameter, and that material is nearly all less than 10 microns in diameter. The rate of rounding is affected by the roundness of feed grains. This was shown by running 1000-gm. batches of $-7.925 + 6.680$ -mm. quartz for three and six days in Abbé mills; 3.22 and 3.56 per cent., respectively, of -200 -mesh material were obtained; this indicates that while the first three days contributed 3.22 per cent. of ground product, the next three, which may be considered as having started with a partly rounded feed, contributed only 0.34 per cent., or one-tenth as much.

The logarithmic plot of the screen analysis of the product of the six-day run made with 1000 gm. of $-22.43 + 18.85$ -mm. quartz is given in

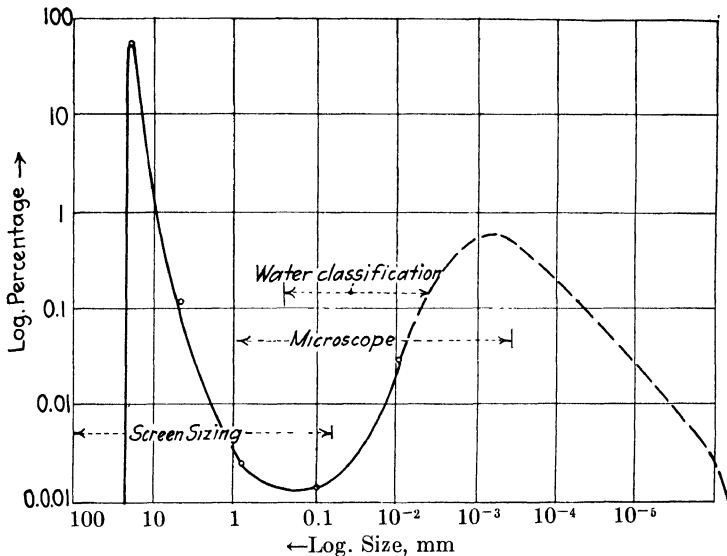


FIG. 25.—WEAR TESTS IN ABBÉ MILL FEED, QUARTZ, THROUGH 22.43, ON 18.85 MM. RUN FOR 6 DAYS AT 51 R. P. M.

Fig. 25. It indicates that after decreasing very rapidly with decreasing size, the percentage amount of product corresponding to a given range in size increases. In order to prove this further, let the 12 per cent. of material less than 10 microns in size be divided equally in as many ranges of size corresponding to a size ratio of 2 as can be accommodated between 10 microns and molecular size (0.5 millimicrons). The range to be divided is $\frac{10}{0.5} = 20,000$. Hence the number of ranges x that can

be accommodated in this range is given by $2^x = 20,000$ or $x = 14$ approximately. Then each range would have $\frac{12}{14} = 0.86$ per cent. of material, which is about ten times as large as the amount (0.098 per cent.) corresponding to the range 0.0092 to 0.0185-mm., and over one hundred

times as large as the amount corresponding to the range 0.208 to 0.417-mm. It may, therefore, be concluded that the logarithmic plot of the sizing analysis, carried beyond the range in which evidence is possible, is somewhat as shown in Fig. 25. On this figure are added, for comparison, the ranges of size in which screen sizing, water classification and microscope sizing are possible.

ROD MILL

In investigating the performance of a rod mill a great many variables enter; the more important are: 1, Speed of mill; 2, rate of feed (duration of run in a batch mill); 3, size of feed; 4, size of rods; 5, quantity of feed; 6, number of rods; 7, size of mill; 8, character of run—intermittent or continuous-discharge or closed circuit with a classifier or screen.

A thorough investigation of these variables would demand a tremendous number of tests, and considerable equipment. In this investigation, all the tests were carried out with a batch mill, consisting of a rotating cylinder 8-in. in diameter and 10 in. long, fitted with a screw base and cap, set on two rollers, one of which was an idler and the other motor driven. The speed of the mill was maintained at 46 r. p. m. The effect of varying the speed of the mill was not investigated because it has, heretofore, received comparatively more attention than other variables.

Shape of Size Curves

The shape of size-curves is given diagrammatically in Figs. 26 and 27, which are the generalized semilogarithmic and logarithmic plots.

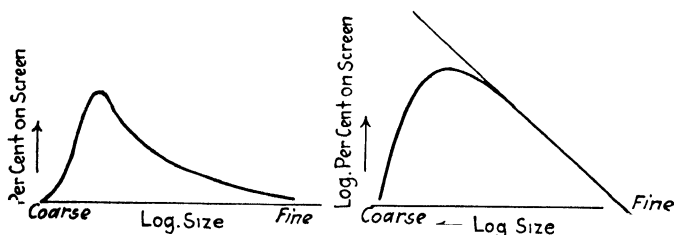


FIG. 26.

FIG. 27.

FIGS. 26 AND 27.—SIZE-CURVES OF ROD-MILL PRODUCT.

It is seen that the straight-line characteristic of the logarithmic plot in roll and jaw crusher is found again in the fine range. In the coarse range the graph becomes a curve with a convexity towards the large percentages, to which the straight-line portion is asymptotic.

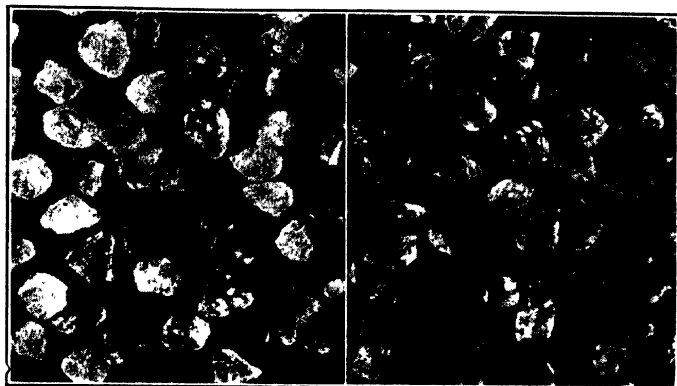


FIG. 28.—ON 2 362 MM.

FIG. 29.—ON 1.168 MM.

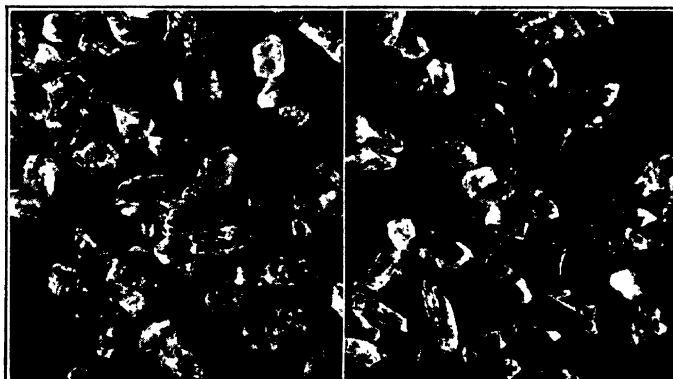


FIG. 30.—ON 0.417 MM.

FIG. 31.—ON 0.147 MM.

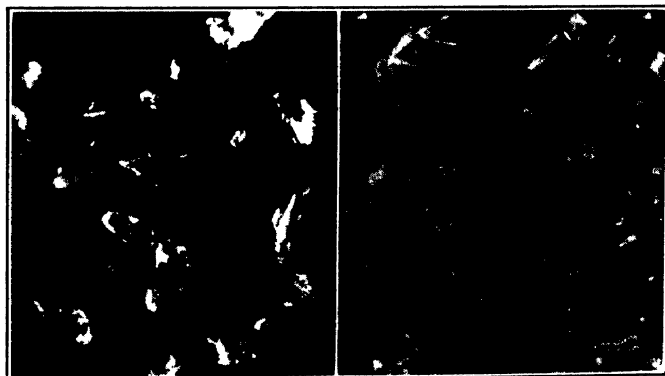


FIG. 32.—ON 0.052 MM.

FIG. 33.—ON 0.018 MM.

ROD-MILL PRODUCTS (QUARTZ).

Shape of Grains

In the fine range, grains are of the same shape as the grains of the fine range of roll product. In the coarse range, on the other hand, they are different; there are no tabular grains and equidimensional grains are common. Some of these even present the appearance of regular polyhedra. While there is no rounding whatever, since sharp corners are the rule, yet the coarse grains look as if all the projecting parts had been chipped off. Figs. 28 to 33, inclusive, show that the fine grains, which correspond to the straight-line portion of the logarithmic plot are similar in shape to the fine grains corresponding to the straight-line portion of the logarithmic plot for roll product, and that the coarse grains are different.

Duration of Run

Runs made in a batch mill for lengths of time which are related by a simple function, give the character of the mill charge at any instant by interpolation between the results obtained and indicate the variations

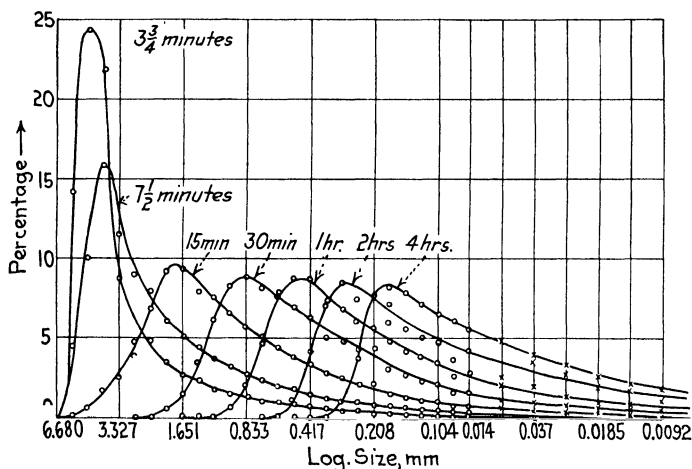


FIG. 34.—SIZE-CURVES OF PRODUCTS OBTAINED BY CRUSHING; QUARTZ THROUGH 6.680 AND ON 4.699 MM. IN A BATCH ROD-MILL FOR DIFFERENT LENGTHS OF TIME.

in character product of a continuous mill for varying rates of feed. Such a series of tests was made with 2500 gm. of $-6.680 + 4.699$ -mm. quartz as feed, and 16 rods $\frac{7}{8}$ in. by 10 in. as the grinding medium. The lengths of time of the various runs were such that each is double the preceding. Fig. 34 shows that as the duration of run increases, the screen-analysis graph moves bodily towards the fine range with but little distortion in shape, after the excess coarse material present at the start has been broken; that is, after some sort of equilibrium condition has been

reached. The maximum height of the curve decreases gradually with increase in time.

If it is desired to know what length of time is required to grind a certain amount of material of a certain size, so that a given percentage be

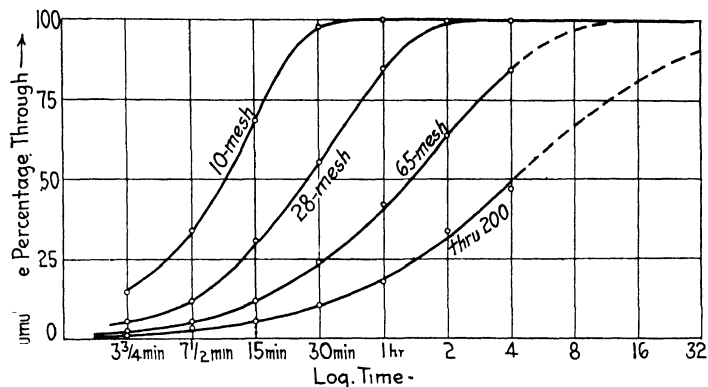


FIG. 35.—FEED, 2500 GRAMS OF QUARTZ, ON 4.699 MM. AND THROUGH 6.680 MM., GROUND IN BATCH ROD-MILL WITH 16— $\frac{7}{8}$ -IN. RODS WEIGHING 14,000 GRAMS AT 46 R. P. M.

finer than a given size, a diagram such as Fig. 35, which, in turn, is obtained from the data pertaining to Fig. 34; should be constructed. Fig. 35 is plotted semilogarithmically; that is, time increases very rapidly

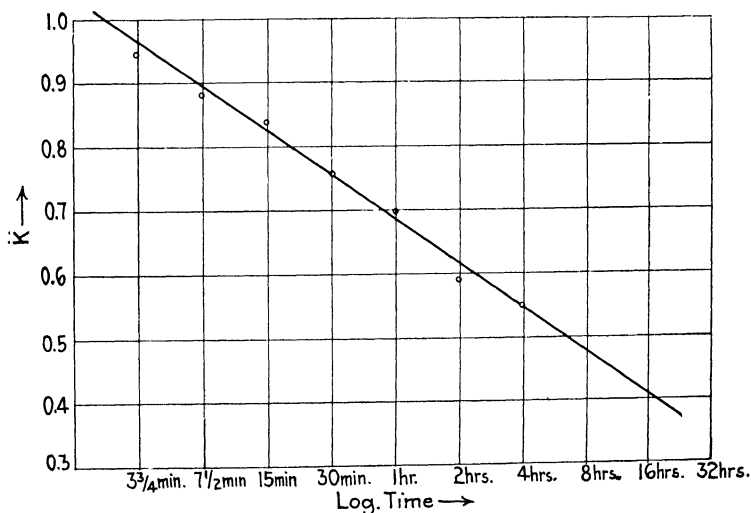


FIG. 36.—FEED, QUARTZ, 2500 GRAMS THROUGH 6.680 AND ON 4.699 MM GROUND IN BATCH ROD-MILL WITH 16— $\frac{7}{8}$ -IN. BY 10-IN. RODS WEIGHING 1,4000 GRAMS AT 46 R. P. M. K VS. LOG TIME.

in going from left to right. In spite of this, the various curves, in going from 0 to 100 per cent. (through) flatten out, having apparently the 100 per cent. ordinate as asymptote. Translated in terms of practical

use, it means that the last traces of a given size are very difficult to eliminate and, for instance, that the time required to grind all through 48 mesh is much more considerable than that required to grind 98 per cent. through 48 mesh.

The value of k decreases directly with the increase in duration of grinding. Fig. 36 shows that k is substantially inversely proportional to log. of time. The physical interpretation is that the fine material increases not only in proportion but also in fineness, as the run is continued. This is, in a way, similar to the increase in fine material that occurs in roll-crushing when the reduction ratio increases.

It is of interest to note that particles up to 6 mm. in diameter can be broken by rods substantially four times that diameter, which would imply a nip angle of $73\frac{1}{2}^\circ$, and a coefficient of friction of 0.86.⁵ Such a coefficient of friction is much larger than the accepted value for the coefficient of friction between rock and metal which is given by Peele^{5a} as 0.3 to 0.7. Richards further states that a value near 0.3 is more nearly acceptable. It must therefore, be concluded that nipping of grains is accomplished by rods when they are not in contact. Assuming a coefficient of friction of 0.3, that is a nip angle of 33° , a rock grain of diameter d , rods of diameter $4d$, the distance between rods, x , is $0.8d$, which is almost as large as the pieces to be broken themselves. Rod mills are usually slow, as compared with ball mills. Their speed is low enough so that the rods roll on each other rather than impinge; in fact there must be rock grains between the rods in order to allow the grains to be nipped, if the usual value for the coefficient of friction between rock and metal is accepted. This situation within the mill causes protection against crushing of fine grains by coarse grains; hence the well-sized character of rod mill product.

It should be noted that in these tests rods frequently became hopelessly tangled at the start of the test, in which case the test was discarded, but that when the beginning was successful, the test ran on smoothly. The noise made by the mill, which is very rough at the beginning of the operation, becomes markedly softer as time progresses. The change in the character of the noise is substantially simultaneous with attainment of equilibrium condition of mill charge (see Fig. 34). These phenomena remain to be explained.

Number of Rods

Within the limits of experimentation, an increase in the number of rods increases the grinding much more than proportionately. In comparing two series of tests in which the number of rods were 4 and 16, the work increased approximately twentyfold. If it be assumed that in a

⁵ For this computation see R. H. Richards: *Ore Dressing* (1903-1909) p. 60.

^{5a} Robert Peele: *Handbook of Mining Engineers*, p. 1961.

rod mill the work is done by impact, this result may be expected, as each one of the 16 rods can encounter 15 rods instead of 3—five times as many—and that there are 16 rods instead of 4—four times as many—hence that the total number of encounters is 20 times as large. This line of reasoning is analogous to that which has been used to determine the

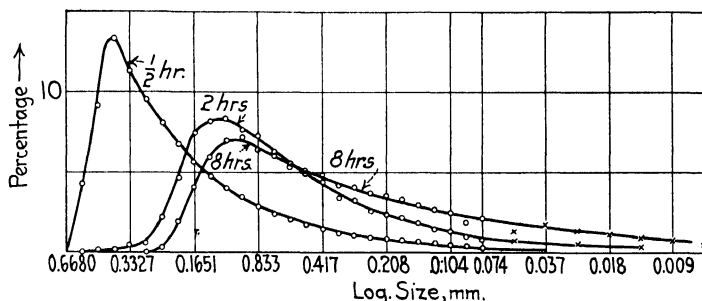


FIG. 37.—FEED 2500 GRAMS OF QUARTZ GROUND IN A BATCH ROD-MILL REVOLVING AT 46 R. P. M., WITH 4—7 $\frac{1}{8}$ -IN. BY 10-IN. RODS WEIGHING 3500 GRAMS. TIME AS SHOWN ON DIAGRAM.

frequency of collision of molecules of gas in a given space and which is $n(n-1)$, or approximately n^2 , when n (the number of molecules) is large. If it be considered that crushing is not done by impact but by rolling of the rods on each other, it may be argued that the load on the material at the bottom of the mill (where the shearing is presumably accomplished) is four times larger when 16 rods are present instead of 4, and that the area on which shearing takes place is five times larger, since there are 15 contact zones instead of 3, so that the work done should again be 20 times larger, or increase roughly as the square of the number of rods. The energy expended in doing this useful work does not increase as the square of the number of rods, but rather less than directly as the number of rods, which form the load of the mill. This indicates that grinding with increased rod load will increase faster than power consumption, up to an undetermined limit. The same conclusion is arrived at by A. F. Taggart⁶ in tests with a ball mill.

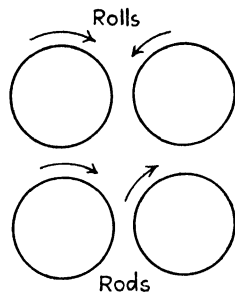


FIG. 38.—DIAGRAM OF ROTATION OF ROLLS AND

As far as the conditions investigated are concerned, it may be concluded that grinding in a rod mill is done by breaking through the grain as well as in a jaw crusher or crushing rolls. The resemblance to rolls is considerable, except that in a rod mill, adjacent rods revolve in the same

⁶ A. F. Taggart: Tests on the Hardinge Conical Mill. *A. I. M. E. Trans.* (1918) 58, 126.

direction instead of in opposite directions, setting up stresses of a different nature from those that are set up in rolls. (Fig. 38). This may be the reason that in rod milling the peak of the curve in the logarithmic plot does not rise above the extension of the straight-line portion, and for the absence of breaking by transverse cracks suggested by this difference in the logarithmic plots of the size tests.

BALL MILL

The following conditions of ball mill operation are variables, and have an effect on the product: 1. Speed of mill; 2, rate of feed (duration of run in the case of a batch mill); 3, weight of charge (this applies to a batch mill); 4, size of balls; 5, size of feed; 6, weight of balls. The size of mill and the character of operation—*i. e.*, continuous-discharge or batch

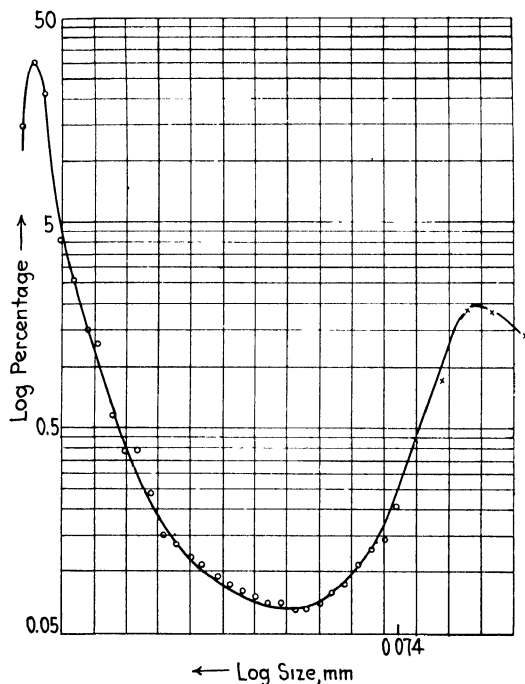


FIG. 39.—FEED, 2500 GRAMS OF QUARTZ THROUGH 13.33 MM. AND ON 9.423 MM., GROUND FOR 4 HR. IN BATCH BALL-MILL WITH 55— $\frac{7}{8}$ -IN. BALLS WEIGHING 3,500 GRAMS.

or in closed circuit with a classifier or screen—also may affect the characteristics of the product.

Most of the tests were carried out in batch mills; where feed and discharge were continuous, the fact is especially noted.

Effect of Size of Feed Grains

The straight-line relation between the logarithm of the percentage corresponding to a certain range in size and the logarithm of that size,

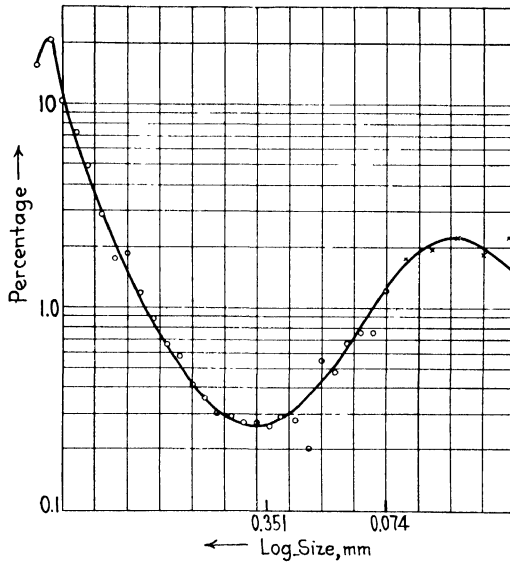


FIG. 40.—FEED, 2500 GRAMS OF QUARTZ, THROUGH 9.423 MM. AND ON 6.680 MM., GROUND FOR 4 HR. IN BATCH BALL-MILL WITH 55— $\frac{7}{8}$ -IN. BALLS WEIGHING 3500 GRAMS.

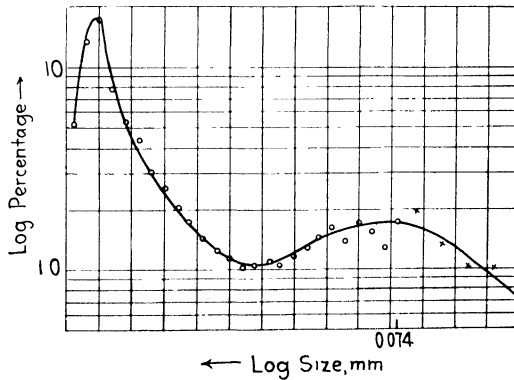
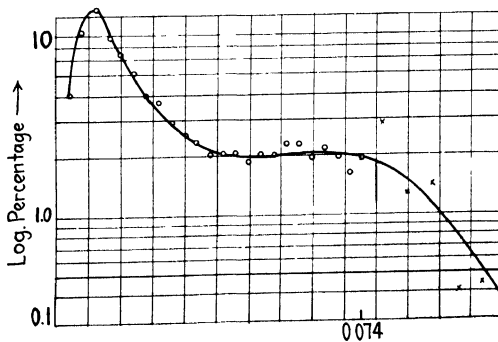


FIG. 41.—FEED, 2500 GRAMS OF QUARTZ THROUGH 6.680 MM. AND ON 4.699 MM., GROUND FOR 4 HR. IN BATCH BALL-MILL WITH 55— $\frac{7}{8}$ -IN. BALLS WEIGHING 3500 GRAMS.



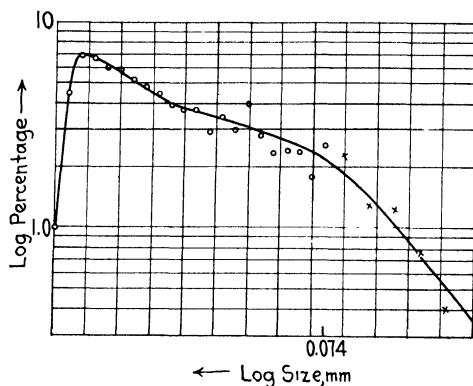


FIG. 43.—FEED, 2500 GRAMS OF QUARTZ, THROUGH 3.327 MM. AND ON 2.362 MM., GROUND FOR 4 HR. IN BATCH BALL-MILL WITH 55— $\frac{7}{8}$ -IN. BALLS WEIGHING 3500 GRAMS.

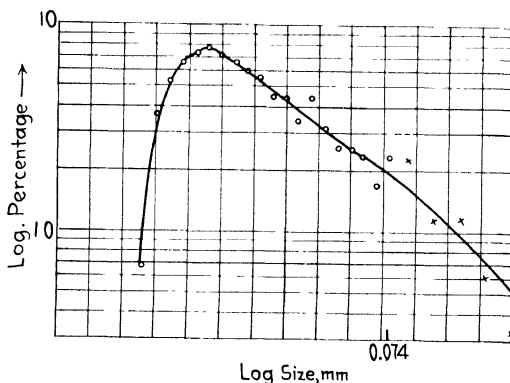


FIG. 44.—FEED, 2500 GRAMS OF QUARTZ, THROUGH 2.362 MM. AND ON 1.651 MM., GROUND FOR 4 HR. IN BATCH BALL-MILL WITH 55— $\frac{7}{8}$ -IN. BALLS WEIGHING 3500 GRAMS.

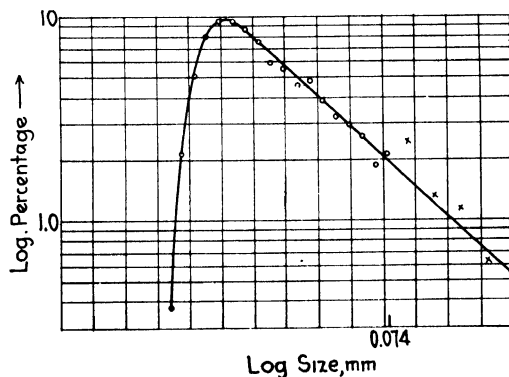


FIG. 45.—FEED, 2500 GRAMS OF QUARTZ, THROUGH 1.168 MM. AND ON 0.833 MM., GROUND FOR 4 HR. IN BATCH BALL-MILL WITH 55— $\frac{7}{8}$ -IN. BALLS WEIGHING 3500 GRAMS.

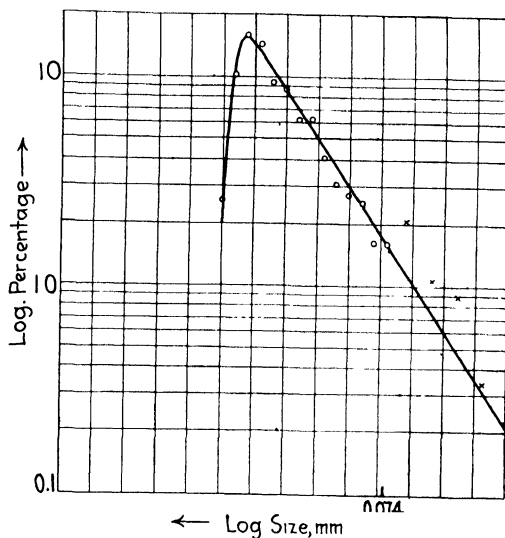


FIG. 46.—FEED, 2500 GRAMS OF QUARTZ THROUGH 0.833 MM. AND ON 0.589 MM., GROUND FOR 4 HR. IN BATCH BALL-MILL WITH 55— $\frac{7}{8}$ -IN. BALLS WEIGHING 3500 GRAMS.

which has been found to hold in the case of the jaw crusher, crushing rolls, and rod mill, holds true in the case of ball milling only under the condition that the ratio of size of feed to size of balls be below a certain critical ratio. When it is above that ratio, the balls appear to grind grains of intermediate size, chipping off sharp edges from the larger grains and eventually rounding these, without pulverizing them. Figs. 39 to 46, inclusive, are the logarithmic plots for a series of tests conducted in order to bring out the existence of the critical ratio of size of feed to size of balls. In this series of tests the ratio is in the neighborhood of $\frac{1}{12}$, since, with $\frac{7}{8}$ to 1-in. balls, material over 2 mm. in diameter does not yield the straight-line size-curve in the fine range, which is characteristic of breaking through the grain.

The notion of critical size-ratio may be related to the notion of nip angle⁷ and of coefficient of friction. Let d (Fig. 47) be the diameter of the particle, $12d$ that of the balls that nip it, α the angle of nip, and μ the coeffi-

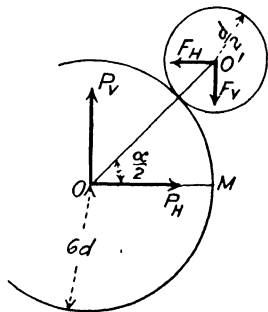


FIG. 47.—DIAGRAM SHOWING RELATION BETWEEN SIZE OF PARTICLE, SIZE OF BALL AND THE NIP ANGLE.

⁷ Alfred T. Fry: A Supplementary Theory of Fine Grinding. *Chem. Eng. & Min. Rev.* (Aug. 5, 1923).

cient of friction. Assuming balls to be touching each other, for nipping to take place, F_v must be less than P_v , F and P being the pressure exerted by the ball and the corresponding friction holding the particle to the ball. The following relations are true:

$$\frac{F}{P} = \mu, \text{ by definition,}$$

$$F_v = F \cos \frac{\alpha}{2}$$

$$P_v = P \sin \frac{\alpha}{2}$$

Hence for $F_v = P_v$,

$$P\mu \cos \frac{\alpha}{2} = P \sin \frac{\alpha}{2} \text{ or, } \mu = \tan \frac{\alpha}{2}$$

But $\frac{\alpha}{2}$ is given by triangle $OO'M$:

$$\cos \frac{\alpha}{2} = \frac{6d}{6d + d} = 0.923, \frac{\alpha}{2} = 22^\circ \frac{1}{2},$$

$$\text{hence } \mu = 0.64$$

This value of the coefficient of friction, based on the assumption that balls come in contact in order to crush is within the limits of 0.3 and 0.7 given by Kent,⁸ Peele⁹ and Richards,¹⁰ but is larger than the value recommended by the latter (0.3). In this connection it should be remembered that square-mesh sieves size grains on their intermediate dimension, while pieces probably become nipped with their smallest dimension normal to the nipping surfaces, so that if the size of grains that are just not nipped were reckoned on their smallest dimension instead of their intermediate dimension, the nip angle and coefficient of friction would appear smaller. Furthermore the feed to the mill in the tests under discussion was made up of roll-product grains, a particularly angular product and one that should, accordingly, show a high coefficient of friction. In the light of these reasons, it appears justified to consider that the critical size observed corresponds to the size of pieces that will just be nipped, and that the corresponding coefficient of friction is 0.64 or less, in agreement with the accepted values for that quantity.

Shape of Product Grains

When the feed does not exceed the critical size for the balls used, the shape of product grains varies with the size considered (very much in the same way as in rod-mill product) that is, the coarser grains are equi-

⁸ R. T. Kent: Mechanical Engineers' Pocket Book.

⁹ Robert Peele: *Op. cit.*

¹⁰ R. H. Richards: *Op. cit.*

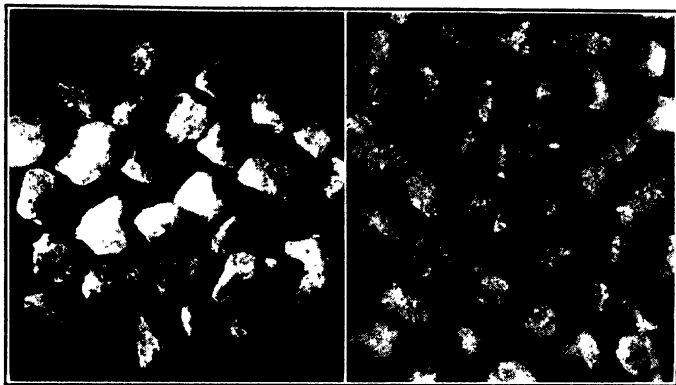


FIG. 48.—ON 9.423 MM.

FIG. 49.—ON 4.699 MM.



FIG. 50.—ON 2.362 MM.

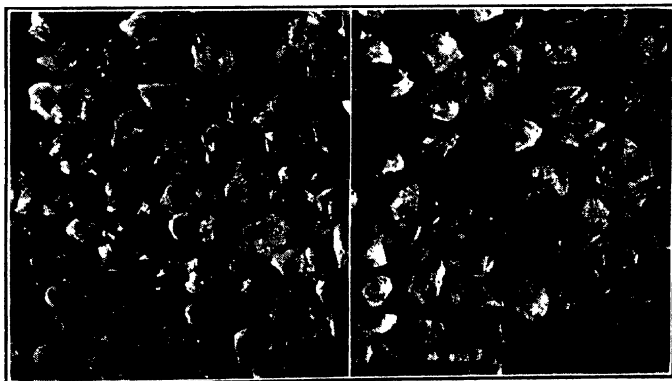


FIG. 51.—ON 1.168 MM.

FIG. 52.—ON 0.589 MM.

BALL-MILL PRODUCTS (QUARTZ).

dimensional or polyhedral and the finer grains are sharp splinters with all gradations between these types. When the critical size is exceeded, the coarse grains become rounded instead of polyhedral, indicating that a wearing process has replaced a disintegrating effect. Figs. 48 to 52 inclusive are photographs of the second coarsest grade made by grinding successively finer feed under otherwise similar grinding conditions and show the gradual change from rounded to polyhedral grains with increase in fineness of feed. Size-curves for the products from which these grains are taken are given in Figs. 39, 41, 43, 45, 46.

Effect of Changing Duration of Run When Feed is Coarser Than Critical Size

The "dip" in the logarithmic or semilogarithmic plots becomes more marked as grinding time is increased, to the point where intermediate sizes may substantially disappear, leaving a product made up of coarse,

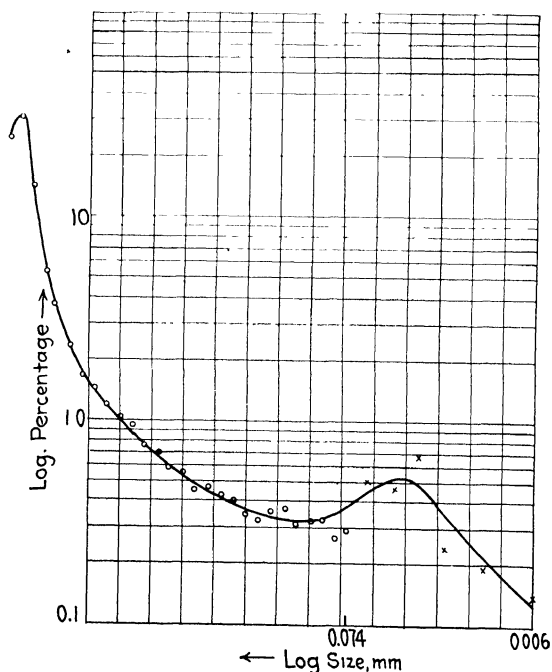


FIG. 53.—FEED, 2500 GRAMS OF QUARTZ, THROUGH 9.423 MM. AND ON 6.680 MM., GROUND FOR 1 HR. IN BATCH BALL-MILL WITH 55— $\frac{7}{8}$ -IN. BALLS WEIGHING 3500 GRAMS.

round fragments (see Figs. 56 to 59 inclusive) and of comparatively very fine, angular grains. Such a product has an appearance totally different from crushed products obtained by other grinding devices, even when due allowance is made for the difference in range of size of grains, but strongly resembles the products of wear tests in Abbé mills, described

previously. The condition realized in the wear tests would appear, therefore, to be a sort of limiting condition which is approximated in ball-milling with feed coarser than the critical size.

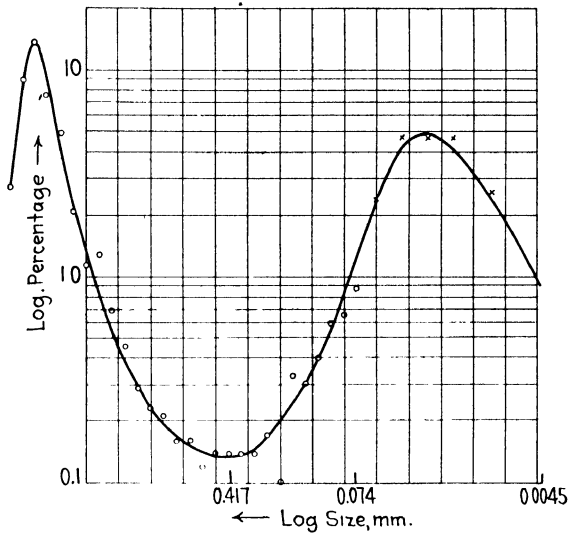


FIG. 54.—FEED, 2500 GRAMS OF QUARTZ, THROUGH 9.420 MM. AND ON 6.680, MM., GROUND FOR 16 HR. IN BATCH BALL-MILL WITH 55— $\frac{7}{8}$ -IN. BALLS WEIGHING 3500 GRAMS.

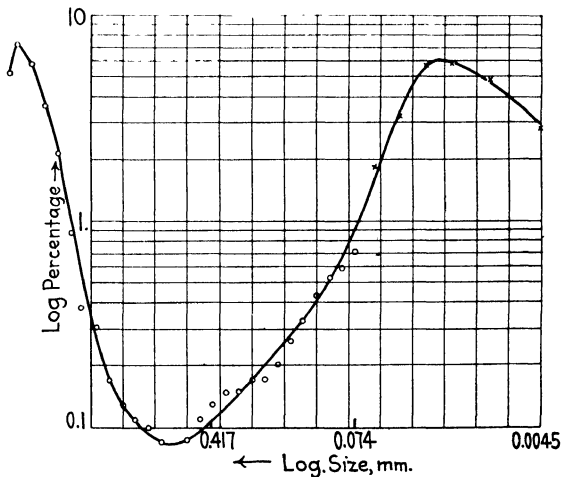


FIG. 55.—FEED, 2500 GRAMS OF QUARTZ, THROUGH 9.423 MM. AND ON 6.680 MM., GROUND FOR 60 HR. IN BATCH BALL-MILL WITH 55— $\frac{7}{8}$ -IN. BALLS WEIGHING 3500 GRAMS.

In the tests in which the feed exceeds the critical size, with respect to ball size, with increased duration of run in a batch mill (corresponding to decreased rate of feed in a continuous mill), the bump that follows the dip in the logarithmic size plot (Figs. 53, 40, 54, and 55) becomes more accen-

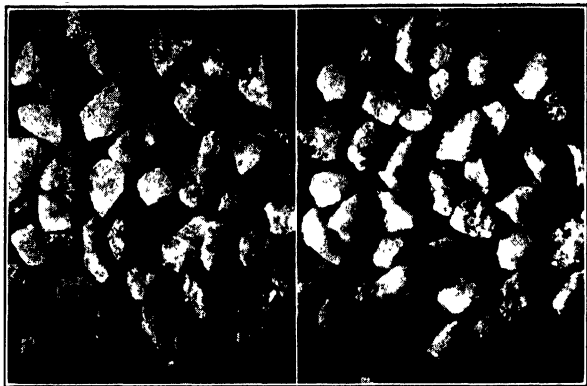


FIG. 56.—1-HOUR RUN.

FIG. 57.—4-HOUR RUN.

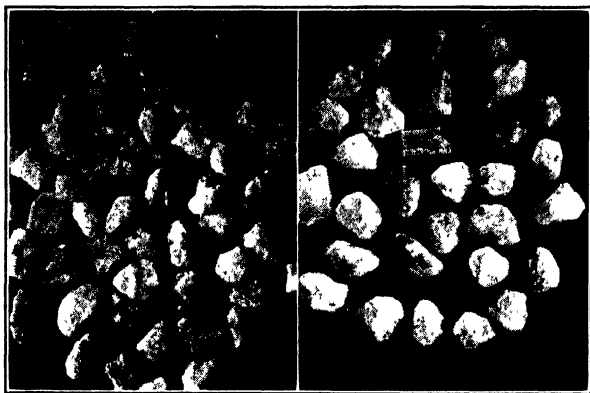


FIG. 58.—16-HOUR RUN.

FIG. 59.—60-HOUR RUN.

BALL-MILL PRODUCTS (QUARTZ).

(ON 6.680 AND THROUGH 7.925-MM. GRADE FROM FEED ON 6.680 AND THROUGH 9.423 MM.)

tuated and moves slightly toward the fine range (Fig. 60). The size corresponding to that bump may be referred to as the size of preponderant breaking for quartz, under the conditions of the test.

The important features that are disclosed by a study of the effect of increasing the duration of grinding in a batch mill with feed of a size exceeding the critical size are:

1. The size of preponderant breaking moves but slightly toward the fine range.
2. Rounding increases in the coarse sizes (Figs. 56 to 59 inclusive).
3. Intermediate sizes decrease in amount.

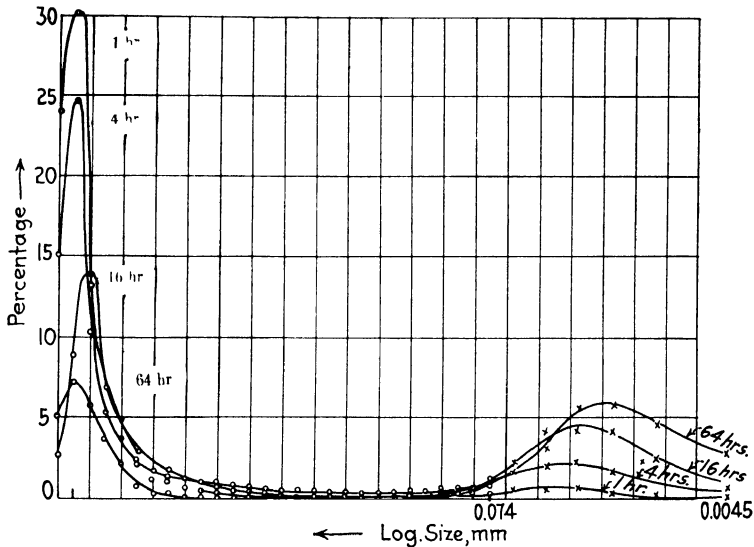


FIG. 60.—FEED, QUARTZ 2500 GRAMS THROUGH 9.423 AND ON 6.680 MM., GROUND FOR DIFFERENT LENGTHS OF TIME IN BATCH BALL MILL WITH 3500 GRAMS OF $\frac{7}{8}$ -IN. BALLS.

Table 2 gives the percentage of quartz of the sizes that can be referred to as coarse, intermediate and fine, for several runs ranging from 1 hr. to 60 hr. made with 2500 gm. of $+6.680$, -9.423 -mm. quartz as feed and 55, $\frac{7}{8}$ to 1-in. steel balls weighing 3500 gm. as the grinding medium.

TABLE 2.—*Percentage of Different Sizes of Quartz after Test Runs of Different Durations*

Size, Mm.	Duration of Run			
	1 hr	4 hr	16 hr.	60 hr
$+2.362$	83.4	64.5	41.5	25.2
-2.362	9.3	6.5	3.0	2.1
$+0.147$				
-0.147				
	7.3	29.0	55.5	73.7

This shows that the percentage of intermediate-size material decreases steadily and that the percentage of fine material increases at first substantially in proportion to time, then more slowly. Fig. 61 is a semi-logarithmic representation of the results of Table 2.

From the results presented, it would seem that with feed coarser than the critical size the balls get a grip on the edges of the angular feed grains (roll product), chipping these off, and making grains of all sizes from feed size down; as time goes on, the coarser grains present fewer and fewer sharp edges that can conveniently be chipped, these edges become smaller, until they are so small that the comminution becomes "wear" instead of "fracture;" at the same time, balls unable to break the larger grains pick on the next finer, and so on; the remaining grains become increasingly difficult to reach, because of their great number and small size and because of cushioning effects. The result is the formation of a preponderant

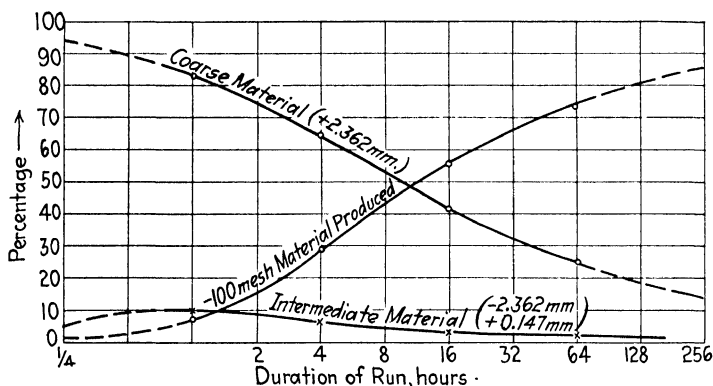


FIG. 61.—FEED, 2500 GRAMS OF QUARTZ, THROUGH 9.423 MM. AND ON 6.680 MM., GROUND FOR DIFFERENT PERIODS IN BATCH BALL-MILL WITH 55 $\frac{7}{8}$ -IN. BALLS WEIGHING 3500 GRAMS. MILL REVOLVING AT 46 R. P. M.

weight of angular grains of a certain size range which is here called the size of preponderant breaking, along with rounded grains of the size or just finer than the size fed to the mill. If the size of feed is less than the critical size, it appears that the grains are broken in order from coarse to fine, so that a situation arises which is totally different from that described above, and which is, in the main, analogous to that which arises in a rod mill.

Size of Balls

In the tests described, run with $\frac{7}{8}$ to 1-in. balls, the critical size was found to be in the neighborhood of 2 mm. With balls twice that size (that is $1\frac{3}{4}$ to 2 in. in diameter), the critical size should be at about 4 mm. In fact, with $-4.699, +3.327$ -mm. quartz, a substantially normal curve is obtained (similar to that obtained with $-2.362, +1.651$ -mm. quartz and $\frac{7}{8}$ to 1-in. balls (Fig. 45), but with $-9.423, +6.680$ -mm. material an

abnormal curve occurs, indicating that the critical size is near 4.6 mm. At the same time, the size of preponderant breaking (for 4-hr. runs) has become coarser, being about 0.052 mm. instead of about 0.026 mm.; that is, twice as much. More experimentation is desirable in this direction, but even with these meager data, it would appear that the size of preponderant breaking is roughly proportional to the ball diameter, and that it is of the order of $\frac{1}{1000}$ of the ball diameter. Accordingly, with 4-in. balls, which are in common use in practice, the size of preponderant breaking should be in the vicinity of $\frac{1}{10}$ mm. (150 mesh) and the critical size about 8 to 10 mm. With 1-in. material as feed, a portion of it would be crushed and another portion worn down, with the result that a few pieces would become rounded, hence difficult to nip, and go around and around in the mill-classifier circuit. This rounded oversize or "tramp" oversize is undesirable. Its disposal is the object of a recent paper.¹⁰ It is customary, in practice, to speed up the mill when coarser feed is employed. This may be successful because of a dependence of critical size on speed.

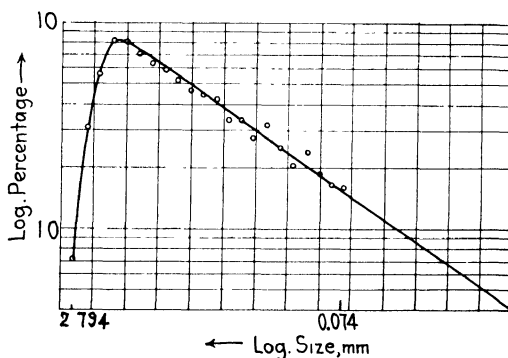


FIG. 62.—FEED, QUARTZ, 120 LBS. PER HOUR, THROUGH 3.327 MM. AND ON 1.651 MM., GROUND IN 20-IN. HARDINGE CONICAL MILL FITTED WITH STANDARD FEED AND DISCHARGE CONICAL SECTIONS AND ONE 18-IN. CYLINDRICAL SECTION; GRINDING MEDIUM 100-3-IN. STEEL BALLS WEIGHING 400 LBS.

Continuous-discharge Mills

A few tests were made in a 20-in. Hardinge conical mill fitted with 100 3-in. steel balls weighing 400 lb. The mill used in this test was composed of standard conical parts for feed and for discharge and of one 18-in. cylindrical portion. The runs were made dry, starting with an empty mill, which was gradually loaded up at the desired rate. A sample of the product discharged was taken after equilibrium had been attained. The results are given in Figs. 62 and 63 for two runs. It is seen that a straight-line relation exists between the logarithms of the percentage

¹⁰ Davis, Willey and Ewing: Recent Developments in the Fine Grinding and Treatment of Witwatersrand Ores. *A. I. M. E. Trans.* (1925) **71**, 983.

retained by each screen and corresponding screen aperture, in the fine range, as would be expected from the data concerning batch mills for feed that is finer than the critical size. Fig. 63 shows that a straight-line relation appears also in the coarse range. The explanation and significance of this relation remain to be found.

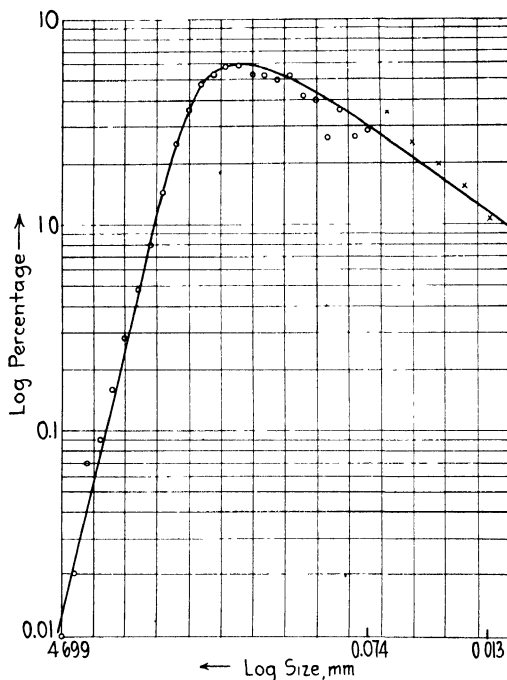


FIG. 63.—FEED, QUARTZ, 60 LBS. PER HOUR, THROUGH 6.680 MM. AND ON 3.327 MM., GROUND IN 20-IN. HARDINGE CONICAL MILL FITTED WITH STANDARD FEED AND DISCHARGE CONICAL SECTIONS AND ONE 18-IN. CYLINDRICAL SECTION; GRINDING MEDIUM 100-3-IN. STEEL BALLS WEIGHING 400 LBS.

Résumé

Crushing in a ball-mill is effected both by breaking through the grain and by wear. Breaking through the grain takes place when the grain is small enough to be nipped by the balls, and wear when the grain is too large to be nipped by the balls.

APPLICATION OF THE RELATION BETWEEN SIZE OF PARTICLE AND PERCENTAGE CORRESPONDING TO A CERTAIN SIZE

The relation $y = Cx^k$ has been found to hold true for the fine range of roll product, jaw-crusher product, and rod-mill product under all conditions tested, and for ball-mill product under certain conditions. In this relation x denotes respectively size; y denotes percentage corresponding to the size-range x to px (where p is the screen ratio or, more

generally, the size ratio); C , a constant depending on the units chosen; and k a constant independent of the units chosen and which, geometrically, is the slope of the straight line in the logarithmic plot.

Discussion of -200-mesh Material

This category comprises all grains that pass a 200-mesh sieve; that is, one having an aperture of 0.074-mm. This class includes grains as coarse as 0.074 mm., as well as grains finer than the finest that can be detected under the microscope, that is 0.0003 mm., a range in size greater than that between the apertures of a 1-in. and a 200-mesh sieve. It is as objectionable to include in the same class grains that are as different as various -200-mesh grains as to put together 1-in. and $\frac{-150}{+200}$ -mesh material. Classifying in water material passing a 200-mesh sieve will give information as to its size to about 0.010 mm., or perhaps to 0.005 mm., but the material finer than that limit will still cover a vast range of sizes and be open to the same objection, although to a lesser extent, than the objection to which is opened unsized -200-mesh material.

In this connection it is important to know how fine solid particles can be. It is well known that matter, in the usual sense of the word, cannot exist in particles more discrete than molecules (if they are compounds) or atoms (if they are elements). According to x -ray data on crystal structure the smallest grain of solid is one that contains at least enough atoms to form a simple crystal of the required crystallographic shape; in the case of galena it is a grain made up of four atoms of lead and four of sulfur (octahedron or cube); such a grain has a diameter of 0.38×10^{-7} mm. Unit crystals are generally more complicated than the galena unit crystal; rarely, however, will they contain over 100 atoms.

The range in size of unit crystals is from 2 to over 10×10^{-7} mm. Assuming 15×10^{-7} (1.5 millimicrons) as the smallest solid grain capable of existence, it is found that the range covered by -200-mesh material is from 0.074 mm. (74 microns or 74,000 millimicrons) to 0.0000015 mm., a range in which the largest grains have 50,000 times the diameter of the finest and of which a 10-story building and a sand grain give a fair size comparison, within reach of our senses of perception.

Let $Y_{1\ 5\mu\mu}^{74,000\mu\mu}$ be the total amount of material finer than the 200-mesh sieve. $Y_{1\ 5\mu\mu}^{74,000\mu\mu}$ is known from weighing the undersize of the finest screen in making a screen analysis, but it can also be obtained by extrapolation of the straight-line relation between $\log x$ and $\log y$. The closeness of the check between $Y_{1\ 5\mu\mu}^{74,000\mu\mu}$ observed and computed should be a measure of the validity of the extrapolation. Table 3 gives a list of the

values of Y observed, Y computed, $\frac{Y \text{ comp't'd} - Y \text{ obs'd}}{Y \text{ obs'd}} \times 100$, and

average $\frac{Y \text{ comp't'd} - Y \text{ obs'd}}{Y \text{ obs'd}} \times 100$. Table 3 shows that the average

difference between the computed and observed percentage of -200-mesh material is less than 4 per cent. of that percentage, a comparatively small amount. It seems, therefore, that the proposed extrapolation is justified. Table 3 shows, furthermore, that the plus errors correspond to jaw crusher and roll tests in which the free discharges induce high atmospheric losses of the very fine material. The minus errors, on the other hand, are located in tests with the Braun pulverizer, rod-mill and ball-mill and

TABLE 3.—*Computed and Observed Percentages of Material*

Per Cent. -200-mesh		$\frac{Y \text{ comp't'd} - Y \text{ obs'd}}{Y \text{ obs'd}} \times 100$	Machine
Actual	Computed		
0 55	1 04	+47	Rolls
1.76	2 38	+24	Rolls
2.05	1 47	-40	Braun pulverizer
4.07	3 71	-10	Braun pulverizer
4.14	3 28	-26	Braun pulverizer
3.28	2.57	-27	Braun pulverizer
3 11	2 44	-27	Rod mill
1.92	1.75	-10	Ball mill
1.03	1 30	+21	Jaw
1.33	1.15	+ 8	Rolls
1 32	1.79	+26	Rolls
1.53	2 05	+25	Rolls
2.42	3.08	+21	Rolls
0.78	1.48	+47	Rolls
0 55	0 71	+23	Rolls
7 81	6 89	-14	Braun pulverizer
7.98	6.89	-16	Braun pulverizer
7 20	6 36	-13	Braun pulverizer
3.00	2.51	-20	Braun pulverizer
0.65	.86	+24	Rolls

may be partly caused by the addition of metal ground from the crushing plates, rods or balls, as the case may be. $Y_{15 \mu}^{74,000 \mu}$ can be computed either by integration or as follows: Consider the straight-line portion of a crushing diagram. Values of y for consecutively smaller values of x , decrease rapidly. Let s be the number of consecutive x 's required to cut the value of y to $\frac{1}{10}$ the value of the first y . It will require another s x 's to cut the value of y to $\frac{1}{100}$ the value of the first y and another s x 's to cut it to $\frac{1}{1000}$; the sum of the y 's corresponding to each cycle of s x 's will be in direct proportion to the ratios $1: \frac{1}{10}: \frac{1}{100}: \frac{1}{1000}$,

etc., which is a rapidly converging series. The total of these numbers is $\frac{10}{9}$. Hence the rule: to get the percentage of material finer than the finest size to which analysis is carried, extend the logarithmic plot and add the percentages corresponding to consecutive size ranges until one individual percentage is approximately equal to $\frac{1}{10}$ of the first percentage recorded. Leave out this last percentage and divide the sum obtained by 0.9.

Average Size of -200-mesh Particle

The knowledge of the proportions of grains of various sizes in -200-mesh material, secured by extrapolation of the logarithmic plot of the screen-analysis of that product, allows accurate computation of the average size of this material in function of k . Before making this computation, however, it is necessary to decide on what basis the average size will be computed. In this connection a paper recently published by W. M. Weigel,¹¹ presents a most interesting and well-taken discussion of the various means of computing average sizes. The average particle can be defined thus:

1. It is a particle such that its diameter multiplied by the total number of particles is equal to the sum of the diameters of all the particles.
2. It is a particle such that its surface multiplied by the total number of particles is equal to the sum of the surfaces of all the particles.
3. It is a particle such that its volume multiplied by the total number of particles is equal to the sum of the volumes of all the particles.
4. It is a particle such that if all the sample were made up of particles of that size, the product of the weight of the sample by the average size would be equal to the sum of the products of the weights of each size by that size.

Consider a lot made up of one cubical particle of diameter $10d$ and 1000 particles of diameter d . The weight of the large particle is $1000gd^3$ and of the small particles $1000gd^3$ where g is the specific gravity. The average size as defined by 1, 2, 3, 4 is respectively:

1. $x \times 1001 = 10d + (1000 \times d) = 1010d$	$x = 1.009d$.
2. $6x^2 \times 1001 = 600d^2 + 6000d^2$	$x = 1.05d$.
3. $x^3 \times 1001 = 1000d^3 + 1000d^3$	$x = 1.26d$.
4. $(2000gd^3)x = (1000gd^3)(10d) + (1000gd^3)(d)$	$x = 5.5d$.

These results indicate that the expression "average size" should be more specifically defined. It is here suggested that it be restricted to

¹¹ W. M. Weigel: Size and Character of Grains of Nonmetallic Mineral Fillers. U. S. Bureau of Mines *Tech. Paper* 296 (1924), 44 pp.

the quantity obtained by the fourth method given above. It should be noted that there is no physical meaning to that quantity except that it is the way in which average size of material is judged by the eye, which weighs bulk of material of a certain size and diameter of particle, that is mass, while there is a definite meaning attached to size of average surface and to a lesser extent to the size of average diameter and the size of average volume. In computing the work done in crushing, the "average size" of -200-mesh material has frequently been taken at 0.037 mm. (one-half the aperture of the 200-mesh screen). This value is slightly smaller than the average size computed by the fourth method given above for $k = 0.8$. On the other hand, it is many times as large as the size of average surface. With $k = 0.8$ for instance, the size of average surface is 0.002 mm.; with $k = 0.6$, it becomes 0.0005 mm., respectively $\frac{1}{18}$ and $\frac{1}{72}$ of the average size (0.037 mm.) commonly ascribed to -200-mesh material.

Computation of Specific Surface, Size of Average Surface, Size of Average Volume and Number of Particles

Let y be the per cent. by weight of material varying from x to px millimeters, z be the per cent. of material per millimeter increase in size, s be the surface of broken material if all particles were cubical, S the real surface of broken material, r_x the ratio between the real surface of the particles of a lot of size x , to the surface of cubical particles having the same "size." By definition

$$(3) \quad S_x^{x+dx} = s_x^{x+dx} r_x$$

If r_x is a constant or substantially so, for all ranges of size:

$$(3') \quad S = r.s.$$

In this paper r will be considered as constant, although it is suspected that it varies. It is proposed to compute s from the screen analysis of a certain material. From the fundamental relation:

$$(2) \quad y = C x^k,$$

the amount of material dz ranging in size from x to $x + dx$ will be dx

$$(4) \quad dz = \frac{C}{p-1} x^{k-1} dx;$$

In a volume of 100 c. c. of material, the volume of material ranging in size from x to $x + dx$ is dz . This volume contains $dN = dz \cdot \frac{10^3}{x^3}$ cubes of edge x , or:

$$(5) \quad dN = \frac{10^3 C}{(p-1)} x^{k-4} dx,$$

so that for the range x_1 to x_2 , the total number of particles is

Generally:
$$p - \frac{p-1}{k-3} [x_2^{k-3} - x_1^{k-3}]$$

(5')

The area per particle is $\frac{6x^2}{100}$ sq. cm.; for dN particles of size x , it is:

hence:
$$dx = \frac{60 C [x_2^{k-1} - x_1^k]}{(p-1)(k-1)}$$

Generally:

(6)
$$S_{x_1 x_2}^{x_2} = \frac{6r \cdot 10C}{(p-1)(k-1)} [x_2^{k-1} - x_1^{k-1}]$$

The volume of material ranging from x_1 to x_2 is obtained by integrating (4), which gives:

(7)
$$Z_{x_1}^{x_2} = \frac{C}{(p-1)k} [x_2^k - x_1^k]$$

Hence $S_{x_1 x_2}$, the specific surface that is the surface per unit volume of material, ranging from x_1 to x_2 , according to relation (2), p. 3, is given by:

(8)
$$S_{x_1 x_2} = \frac{S_{x_1 x_2}^{x_2}}{Z_{x_1}^{x_2}} = \frac{6r \cdot 10C [x_2^{k-1} - x_1^{k-1}](p-1)k}{(p-1)(k-1)C[x_2^k - x_1^k]}$$

(8)
$$S_{x_1 x_2} = 60 \cdot r \cdot \frac{k}{k-1} \cdot \frac{x_2^{k-1} - x_1^{k-1}}{x_2^k - x_1^k}$$

where x is expressed in millimeters and $S_{x_1 x_2}$ in square cm. per c. c.

Size of Average Surface—Specific Surface.—Table 4 gives values of $S_{x_1 x_2}$ computed for $r = 1$, various values of k and various $x_1 - x_2$ ranges, x_1 and x_2 are in mm. $S_{x_1 x_2}$ in sq. cm.

TABLE 4.—Values of $S_{x_1 x_2}$ for $x_1 = 1$ mm.

k	Range $x_1 - x_2, (x_2 > x_1)$			
	10	10 ²	10 ³	10 ⁴
0.3	20.84	8.35		
0.4	19.70		2.52	0.402
0.5	18.90			
0.6	18.18	5.10	1.34	0.0895
0.7	17.32			
0.8	16.64	3.72	0.714	0.0206
0.9	15.96	3.21	0.540	0.01164
1.0				
1.1	14.76	2.38	0.328	0.00450
1.2	14.22	2.18	0.269	0.00330
1.3	13.68	1.95	0.227	0.00251

Fig. 64 is a logarithmic plot (drawn on semilogarithmic paper for convenience) giving the value of S_{x_1, x_2} , for various values of k (from 0.3 to 1.3) and of the range $x_1 x_2$. It will be noted, by the way, how these curves fan out with increasing $\frac{x_2}{x_1}$ and how little difference k makes when $\frac{x_2}{x_1} < 4$.

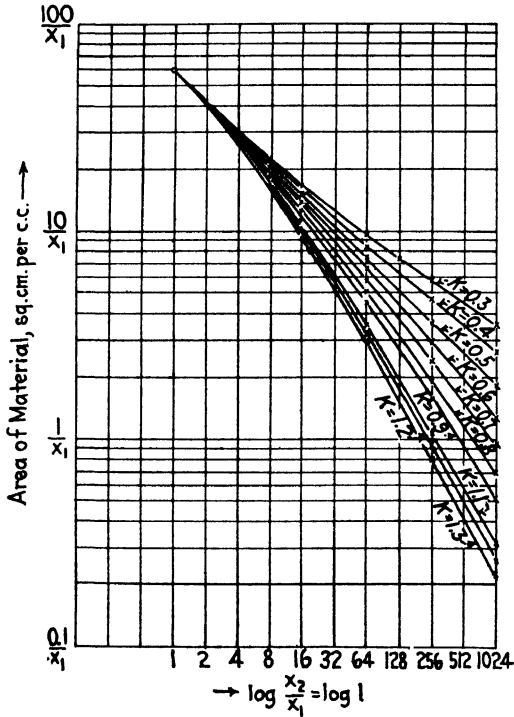


FIG. 64.—AREA OF 1 C.C. OF CRUSHED MATERIAL RANGING IN SIZE FROM x_1 TO x_2 MM.

Application.—Find the area of 500 gm. of a mineral of specific gravity 2.5 for which $k = 0.65$ and for which the grains range in size from 2 microns (0.002 mm.) to 0.2 mm. Assume that the average area per particle is 1.2 times as large as it would be if the particles were cubes.

$$\text{Volume} = \frac{500}{2.5} = 200 \text{ c. c.}$$

since $100, k = 0.65$

$$\text{or,} \quad \sim \quad \frac{4.6}{0.002}$$

$$\text{area} = 200 \times 1.2 \times 4.6 \times 0.002 = 5.5 \times 10^5 \text{ sq. cm.}$$

In order to simplify matters, the area of -200 -mesh material was determined once for all for various values of k . It is given in Table 5, and by Fig. 65.

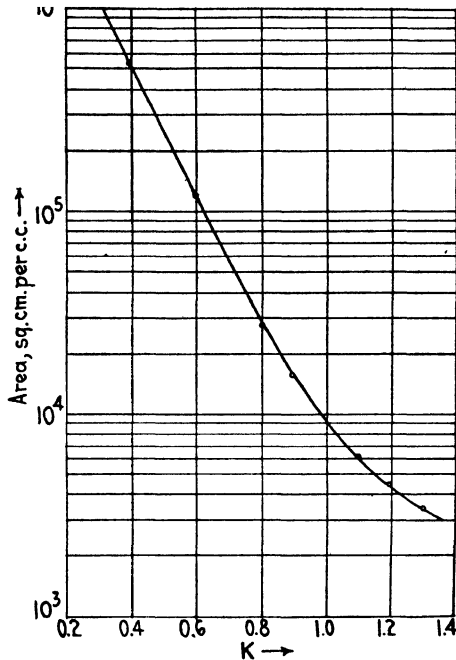


FIG. 65.—AREA OF -200-MESH MATERIAL, $\frac{\text{SQ. CM.}}{\text{C.C.}}$ VS. k .

TABLE 5.—Specific Surface of -200-mesh (0.074 mm.) Material ($r = 1.0$)

	AREA, Sq. Cm.
0.4	54.2 × 10 ⁴
0.6	12.1 × 10 ⁴
0.8	2.78 × 10 ⁴
0.9	1.58 × 10 ⁴
1.1	0.609 × 10 ⁴
1.2	0.447 × 10 ⁴
1.3	0.340 × 10 ⁴

Application.—Find the surface of 500 gm. of -200-mesh material of specific gravity 2.5, in which it is known that $k = 0.75$, $r = 1.4$.

Volume = $\frac{500}{2.5} = 200$ specific surface = 4×10^4 sq. cm. Total area = $1.4 \times 200 \times 4 \times 10^4 = 11.2 \times 10^6$ sq. cm.

The size of average surface can be obtained directly from the specific surface S_{s_1, s_2} as follows: Since the volume occupied by material of surface S_{s_1, s_2} is unity, and the volume of the particle of average surface is $\frac{x_s^3}{10^3}$, and its surface $\frac{6x_s^2}{10^2}$: then (x expressed in millimeters, volume in c. c., surface in sq. cm.)

$$10^{-3}nx_s^3 = 1,$$

where n is the number of particles

$$10^{-2}n \cdot 6x_s^2 = S_{s_1, s_2}$$

of average surface whose volume is unity.

Dividing these equations member to member, $\frac{x_2}{60} = \frac{1}{S_2}$

or

(9) $x_2 = \frac{60}{S_{x_1, x_2}}$ where S_{x_1, x_2} is expressed as square cm./c. c. and x_1, x_2, x_3 in millimeters.

Application.—Find size of average surface of -200-mesh material for $k = 0.4, 0.6, 0.8, 1.0$.

For $k = 1.0$	$= 0.9 \times 10^4$ hence	$\frac{60}{0.9 \times 10^4} = 6.7$
$k = 0.8$	$= 2.8 \times 10^4$ hence	$x_2 = 2.14 \times 10^{-3}$ mm.
$k = 0.6$	$= 12.0 \times 10^4$ hence	$x_2 = 0.50 \times 10^{-3}$ mm.
$k = 0.4$	$= 54.0 \times 10^4$ hence	$x_2 = 0.11 \times 10^{-3}$ mm.

Size of Average Volume

The size of average volume can be obtained as follows: The volume of a cube of edge x is $\frac{x^3}{10^3}$. The volume of dN such cubes would be:

$$\frac{10^3 C}{p-1} \cdot \frac{x^3}{10^3} = \frac{Cx^{k-1}dx}{p-1}$$

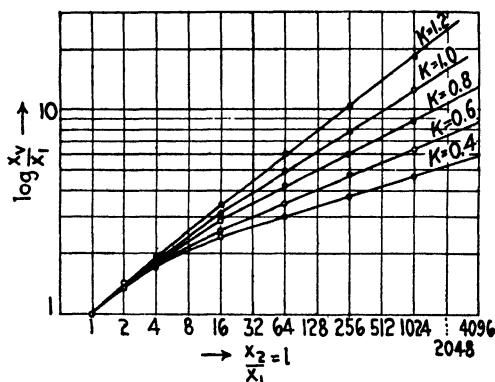


FIG. 66.—SIZE OF PARTICLE OF AVERAGE VOLUME.

$$x_2 = \sqrt[3]{\frac{k-3}{k}} \cdot \sqrt[3]{\frac{\left(\frac{x_2}{x_1}\right)^k - 1}{\left(\frac{x_2}{x_1}\right)^{k-3} - 1}}$$

and the volume $V_{x_1}^{x_2}$ of $N_{x_1}^{x_2}$ particles would be $\int_{x_1}^{x_2} C \frac{x^{k-1} dx}{p-1}$ while

their number would be $\int_{x_1}^{x_2} C x^{k-4} dx$. Hence size of average volume

in millimeters is 10 times the cube root of $\frac{V_{x_1}^{x_2}}{N_{x_1}^{x_2}}$ or,

$$(11) \quad x_v = \frac{p - \frac{10^3 C}{p-1} \int_{x_1}^x}{\sqrt[3]{\frac{x_2^k - x_1^k}{x_2^{k-3} - x_1^{k-3}}}} = \sqrt[3]{\frac{k-3}{k}} \sqrt[3]{\frac{\left(\frac{x_2}{x_1}\right)^k - 1}{\left(\frac{x_2}{x_1}\right)^{k-3} - 1}} \cdot x,$$

Fig. 66 gives values of x_v in terms of x_1 for various values of $\frac{x_2}{x_1}$ and of k . This graph is to be used exactly as Fig. 64.

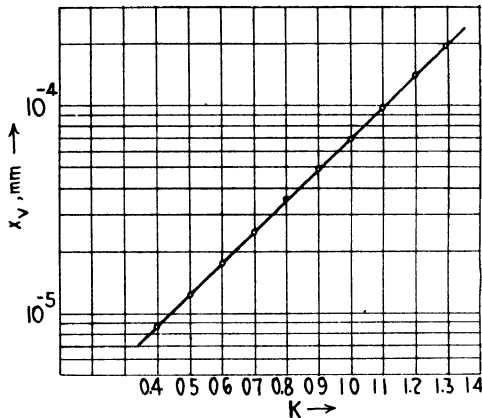


FIG. 67.—SIZE OF PARTICLE OF AVERAGE VOLUME ON 200-MESH MATERIAL.

$$x_v = 1.5 \sqrt[3]{(50,000)^k - 1}$$

For -200-mesh material, putting $x_1 = 1.5\mu\mu$, $\frac{x_2}{x_1} = \frac{74,000}{1.5} = 50,000$ approx. values of x_v in millimeters are given by Fig. 67. The equation x_v, k is very nearly a straight line when plotted on semilogarithmic paper because equation (11) reduces to:

$$(12) \quad 1.5 \sqrt[3]{(50,000)^k - 1},$$

$$\text{or } \log x_v = \log 1.5 + \frac{1}{3} [\log (3 - k) - \log k] + \frac{1}{3} \cdot \log (50,000^k - 1)$$

and that $(50,000)^k$ is generally very large compared to unity.

Definition and Computation of Crushing Efficiency

The work actually used in crushing material is difficult to estimate, because no universally accepted law exists to measure it. As is pointed

out in the literature, a part of the work of crushing is employed to make noise, part to make new surface (surface energy) and part to make heat. Both heat and noise are the result of vibrations set up in solid matter by impact or friction, and are not desired. New surface, on the other hand, is in a way an index of what has been accomplished and new surface energy can be looked upon as a measure of the "useful work" done in crushing. The surface energy developed can be obtained from the specific surface (Figs. 64 and 65) and the specific surface energy of the mineral that is being ground. Edser¹² gives 920 ergs/sq. cm. as the surface

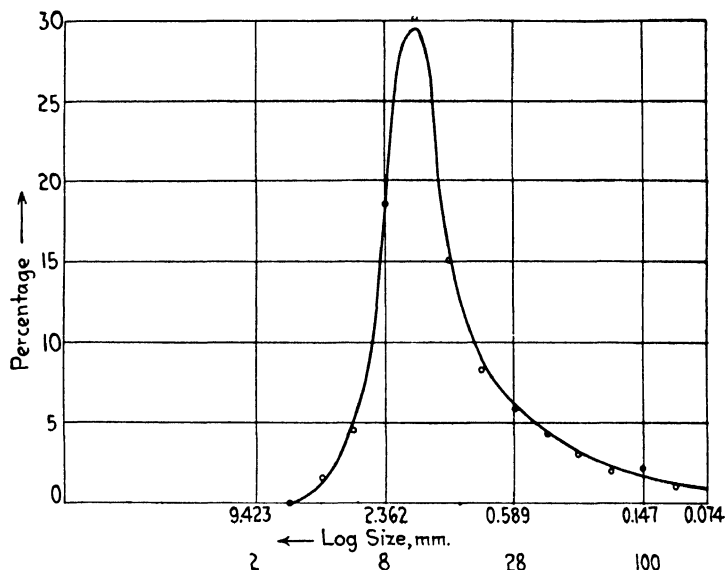


FIG. 68.—REDRAWN FROM FIG. 9 IN PROFESSOR HAULTAIN'S DATA.

energy of quartz. Taking, for instance, the ninth test in Haultain and McNiven's data¹³ on quartz; plotting y vs. $\log x$, drawing curve of best fit and transferring points of intersection of that curve with corresponding ordinates to a $\log y - \log x$ plot, a straight line, $k = 0.92$, is obtained (see Figs. 68 and 69). The amount of -200 -mesh material obtained by extrapolation is $\frac{0.68 + 0.49 + 0.35 + 0.27 + 0.19 + 0.14 + 0.10}{0.9} = 2.47$

per cent., a fair check as compared with 2.30 per cent. actually obtained.

The specific surface of -200 -mesh material for $k = 0.92$ is $0.140 \times 10^4 \frac{\text{sq. cm.}}{\text{c.c.}}$ (Fig. 65); therefore in a 100-c.c. sample of product the area

¹² Fourth Report on Colloid Chemistry and its General and Industrial Applications, 281. British Assoc. for Advancement of Science.

¹³ H. E. T. Haultain and J. C. McNiven: University of Toronto, *Engineering Research Bull.* No. 4, 157.

of -200-mesh material obtained, assuming particles to be all cubical, is $2.3 \times 1.4 \times 10^4 = 3.22 \times 10^4$ sq. cm. The amount of material present follows the $y = Cx^k$ law between the sizes 0.833 mm. and 0.074 mm., or a range of size of $8\sqrt{2}$. Therefore, from Fig. 64, and for $k = 0.92$, the surface of the material is $14.5 \frac{1}{0.074} = 196$ sq. cm./c.c. For a

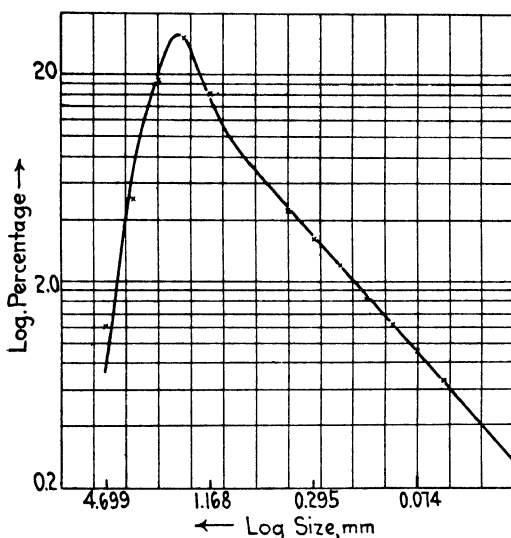


FIG. 69.—LOGARITHMIC PLOT DRAWN FROM FIG. 68.

total percentage of 27.5, the corresponding surface is $196 \times 27.5 = 0.539 \times 10^4$ sq. cm. For the material coarser than 0.833-mm. the surface may be estimated in the usual way, as follows:

Size, Mm.	Surface Sq. Cm. C.c.	Per Cent.	Surface Sq. Cm. C.c.
4.699	12.7	1.6	20
3.327	18.0	4.7	85
2.362	25.4	8.6	473
1.651	36.3	30.2	1097
1.168	51.4	15.1	774
Total.....			2451 or 0.245×10^4

Hence the total surface of +200-mesh material is $(0.539 + 0.245)10^4 = 0.78 \times 10^4$ sq. cm.

The total surface of +200-mesh and -200-mesh material combined is 4.00×10^4 sq. cm./100 c. c. (of which 19 per cent. is accounted for by

the +200-mesh material and 81 per cent. by the -200-mesh material). The total surface in 100 c. c. of feed is $100 \times 12.8 = 1280$ sq. cm. per 100 c. c., therefore new surface is 3.87×10^4 sq. cm. per 100 c. c.

Taking r as 2 (rolls make a very splintery product), the new surface is 7.7×10^4 sq. cm. Corresponding surface energy is $7.7 \times 10^4 \times 0.92 \times 10^3 = 7.1 \times 10^7$ ergs, or

$$= \frac{7.1 \times 10^7}{4.2 \times 10^7} \times \frac{454}{100 \times 2.65} \times \frac{1}{252} \times 778 = 9.0 \frac{\text{foot-lb.}}{\text{lb.}}$$

The new surface energy developed in the rock is but a small fraction of the energy input, which is given¹⁴ for a similar test as about 700 foot-lb. per lb. That is, a very small portion (1.3 per cent.) of the energy input is recovered as surface energy in the product, under the conditions, least wasteful in energy, realized by Professor Haultain. The balance (99 per cent.) of the energy input goes to make heat, noise and frictional losses in bearings and transmission machinery. If it were possible to deduct drive losses, the energy input would divide itself in surface energy (useful work) and heat and noise, which could be considered as the losses of the crushing process itself. This would permit computation of crushing efficiency; not on a relative basis but on the basis of output/input which is truly an efficiency. If in the above instance drive and bearing losses amounted *e. g.* to 500 ft.-lb. per pound of rock, the energy consumed in crushing would be $700 - 500 = 200$ ft.-lb. per lb., and the efficiency E would be 4.5 per cent. It is difficult to determine bearing losses accurately, as these losses depend on the pressure exerted by the rotating shaft, and this pressure in turn is variable and depends on the reaction on the rolls of the pieces that are being broken. If some means of automatically recording the variations of the bearing pressure with time could be devised, it might be possible to eliminate this effect and get at the true crusher efficiency. An efficiency that includes bearing losses, while dependent to a large extent on the quality of the bearings, would be more significant to the practical man. In the present instance, it would amount to

$$E = \frac{9.0}{700} = 1.3 \text{ per cent.}$$

Such a small value as is obtained here is surprising, but it is useful, in this instance, to remember that the efficiency of a good steam engine is only 15 per cent. and that the overall efficiency of a locomotive is rarely much over 4 per cent.

Kick vs. Rittinger

Relative mechanical efficiency is a number presumably proportional to the unknown actual efficiency, when a certain system of units is adhered to.

¹⁴ H. E. T. Haultain: *Op. cit.*, 147.

The relative mechanical efficiency obtained by Rittinger's method should be proportional to the true efficiency as defined above, since Rittinger states that the work done is proportional to the new surface formed. There is, however, a difference between the usual computation of R. M. E., and the computation offered in this paper in that the average size of -200 -mesh material has always been overestimated, making a correspondingly great error in underrating the area of -200 -mesh material and the energy units it represents.

Kick's so-called law states that equal changes in configuration demand equal output of work. Thus to reduce a cube of edge x_f to cubes of edge $\frac{x_f}{2^n}$ would demand n times as much work as to reduce it to cubes of edge $\frac{x_f}{2}$. Hence the work done on the piece of size x_f is proportional to

$\log x_f - \log x$ or to $(D - \log x) - (d - \log x_f)$, $D - \log x$ being looked upon as the work contained in pieces of size x , and $D - \log x_f$ as that contained in pieces of size x_f . For dz per cent. of material, ranging in size from x to $x + dx$, putting $D = 0$, the work contained in the pieces is $dw = -m \log x \, dz$ where m is a constant.

But

$$dz = \frac{C}{p-1} x^{k-1} dx$$

hence

$$dw = \frac{-mc}{p-1} \log x \cdot x^{k-1} dx = -M x^{k-1} \log x \, dx$$

where M is a positive constant, depending upon the units chosen.

The work contained in pieces varying from x_1 to x_2 is $W_{x_1}^{x_2}$.

$$\begin{aligned} W_{x_1}^{x_2} &= -M \int_{x_1}^{x_2} x^{k-1} \log_e x \, dx = -M \sum_{x_1}^{x_2} x^k \left[\frac{\log_e x}{k} - \frac{1}{k^2} \right] \\ &= -\frac{M}{k} \left[(x_2^k \log_e x_2 - x_1^k \log_e x_1) - \frac{x_2^k - x_1^k}{k} \right] \end{aligned}$$

To get the specific work (work per unit volume), $W_{x_1 x_2}$ contained in pieces varying from x_1 to x_2 , $W_{x_1}^{x_2}$ must be divided by the percentage

weight, $z_{x_1}^{x_2} = \frac{C}{(p-1)k} [x_2^k - x_1^k]$ corresponding to the range $x_1 x_2$;

$$\begin{aligned} \therefore W_{x_1 x_2} &= \frac{-mC}{k(p-1)} \left[\frac{x_2^k \log_e x_2 - x_1^k \log_e x_1}{x_2^k - x_1^k} - \frac{\frac{x_2^k - x_1^k}{k}}{x_2^k - x_1^k} \right] \\ &= -m \left(\frac{x_2^k \log_e x_2 - x_1^k \log_e x_1}{x_2^k - x_1^k} - \frac{1}{k} \right) \end{aligned}$$

Let l be the ratio $\frac{x_2}{x_1}$, then $x_2^k = x_1^k \cdot l^k$, $\log_e x_2 = \log_e x_1 + \log_e l$

and

$$= -m \left(\frac{\log_e l - x_1^k \log_e}{x_1^k l^k -} - \frac{1}{k} \right)$$

Simplifying:

$$-m \left[\log_e x_1 + \frac{l^k \log_e l}{l^k - 1} - \frac{1}{k} \right]$$

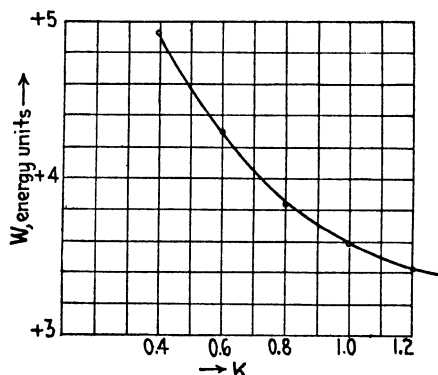


FIG. 70.—ENERGY UNITS CONTAINED IN -200-MESH MATERIAL; BY KICK'S "LAW," W vs. K .

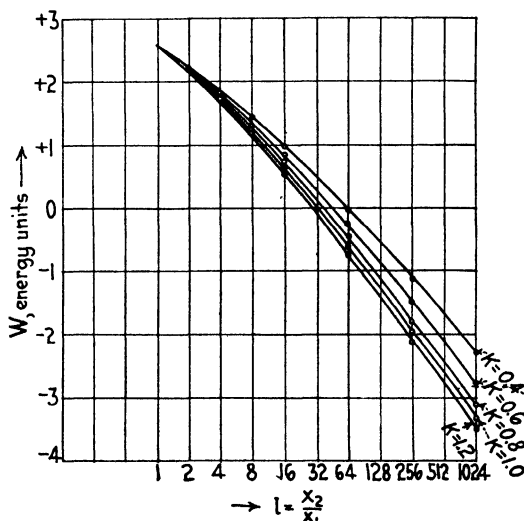


FIG. 71.—ENERGY UNITS CONTAINED IN +200-MESH PARTICLES BY KICK'S "LAW" FOR VARIOUS VALUES OF $\frac{x_2}{x_1} = l$ AND OF k . $x_1 = 0.074$ mm.

For -200-mesh material, $l = 50,000$, $x_1 = 1.5 \times 10^{-6}$ mm. Using logs. to base e , $m = 1$, and x 's in mm., as a consistent system of units, the work represented by -200-mesh material for various k 's can be computed (see Fig. 70).

For +200-mesh material, and various values of l and k , consult Fig. 71.

HETEROGENEOUS ROCKS

Sedimentary rocks are made up of grains of various minerals, bonded by a cement; a weakness is naturally present at the grain boundaries.

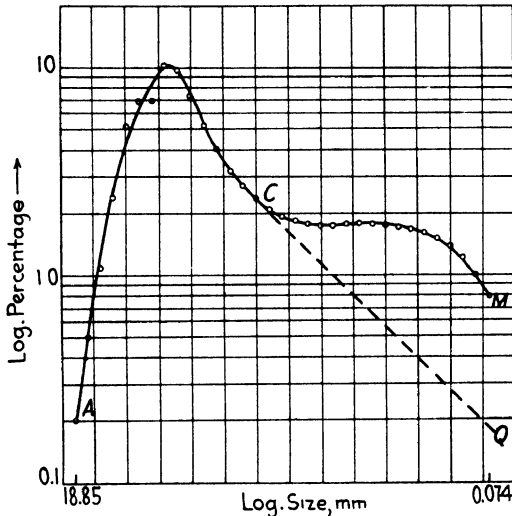


FIG. 72.—FEED: THROUGH 22.43 MM. AND ON 18.85 MM. (MANHATTAN SCHIST PARTICLES WHOSE LEAST DIMENSION IS ON 5.5 MM. AND THROUGH 11.0 MM. TO ROLLS SET AT 5.613 MM.)

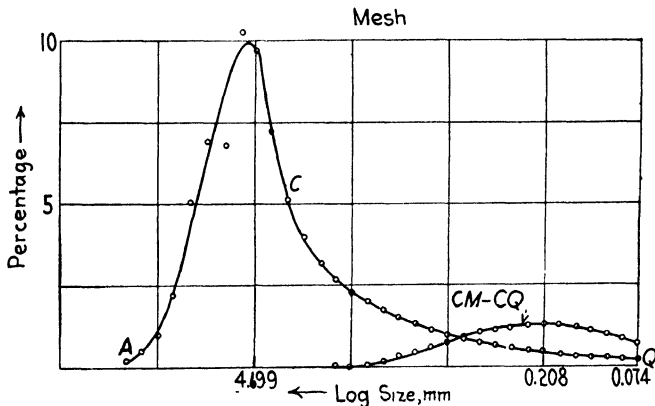


FIG. 73.—REDRAWN FROM FIG. 72.

This weakness is more or less marked, just as the state of aggregation may vary from that of a loose sand to that of a highly indurated quartzite. Igneous rocks are generally fairly homogeneous in character, as can be

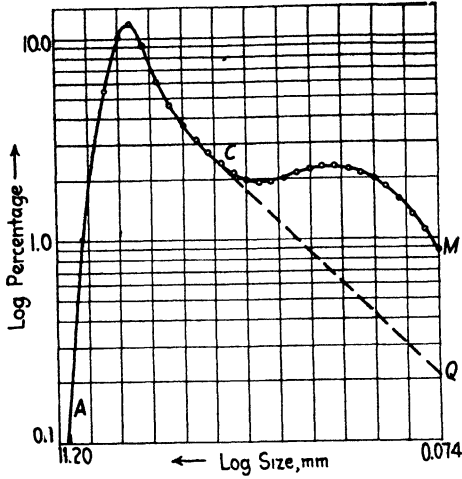


FIG. 74.—FEED, THROUGH 22.43 MM. AND ON 18.85 MM. (MANHATTAN SCHIST PARTICLES WHOSE LEAST DIMENSION WAS THROUGH 14.0 MM. AND ON 11.5 MM. TO ROLLS SET AT 5.613 MM.)

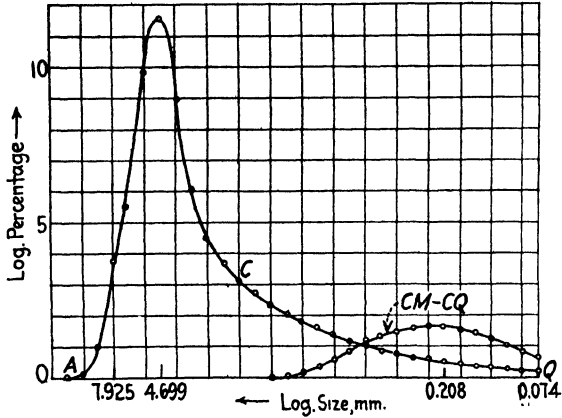


FIG. 75.—REDRAWN FROM FIG. 74.

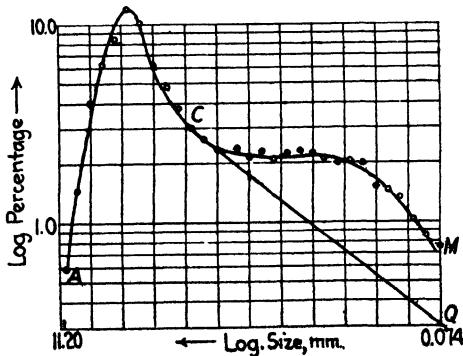


FIG. 76.—FEED, THROUGH 22.43 MM. AND ON 18.85 MM. (MANHATTAN SCHIST PARTICLES WHOSE LEAST DIMENSION IS THROUGH 17 MM. AND ON 14.5 MM., TO ROLLS

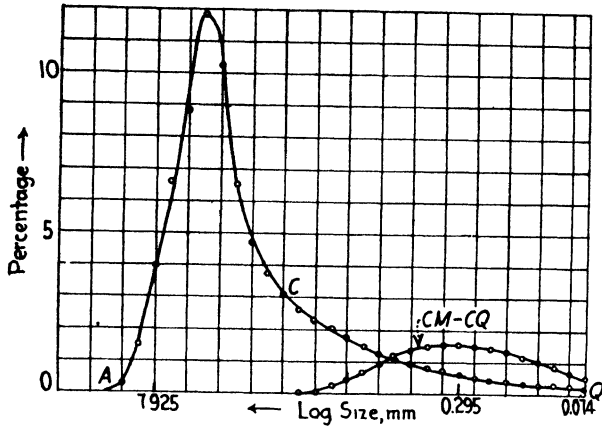


FIG. 77.—REDRAWN FROM FIG. 76.

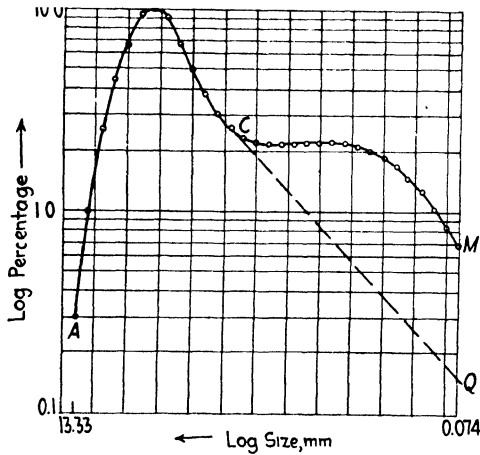


FIG. 78.—FEED, THROUGH 22.43 MM. AND ON 18.85 MM. (MANHATTAN SCHIST PARTICLES WHOSE LEAST DIMENSION IS THROUGH 20 MM. AND ON 17.5 MM. TO ROLLS SET AT 5.613 MM.)

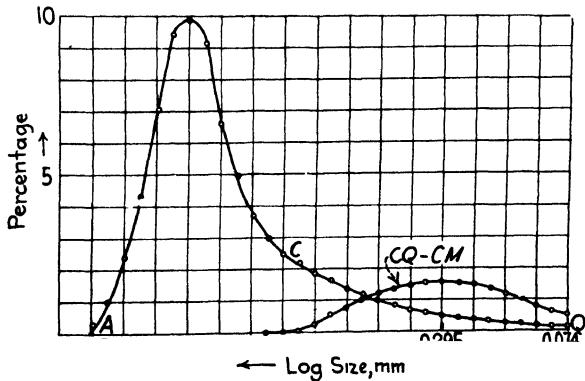


FIG. 79.—REDRAWN FROM FIG. 78.

observed by fracture which takes place through the grains. Metamorphic rocks frequently present a highly heterogeneous structure, particularly if they contain large amounts of micas. Weathered rocks, also, are heterogeneous because the disintegration of the grain-boundary material or cement is generally more rapid under the action of weathering processes.

Manhattan schist is an example of a heterogeneous rock. It is a very ancient sediment now completely metamorphosed into a schist containing micas, feldspars, quartz and a number of less common silicates such as garnet, pyroxene, hornblende, sillimanite, etc. Results obtained in crushing this rock with crushing rolls are given in Figs. 72 to 79 inclusive. These figures should be compared with Figs. 4-10, which represent the results obtained with quartz feed of the same size and with the rolls at the same set.

On the logarithmic plot, the straight line obtained with quartz disappears and is replaced by a curve having a more or less well defined hump. Following one of the logarithmic plots for Manhattan schist, Fig. 78, for instance, from the coarse to the fine range of the diagram, the curve at first is substantially like the curve for quartz. From *C* on, the quartz plot continues in some such fashion as *CQ*, while that for schist is *CM*. If the difference between *CQ* and *CM* is plotted on a semilogarithmic basis, the curve obtained represents fairly well a probability curve. Figs. 73, 75, 77 and 79, show that the "probability curve" referred to above has its maximum in the vicinity of the sizes represented by the 0.208-mm. and 0.295-mm. screens. Of ten tests carried out under different conditions (one jaw-crusher product, one Abbé-mill test, one ball-mill test, one rod-mill test, two disk-pulverizer tests and four crushing-roll tests), four show greatest amount of preferentially broken material at from 0.208 to 0.246 mm., three at from 0.246 to 0.295 mm. and three at from 0.295 to 0.351 mm., averaging at 0.27 ± 0.013 mm.

In order to explain the existence of this size of preferential breaking in this nonhomogeneous rock and to relate it with the average grain size of the rock, a dimensioned count of grains was made in several photomicrographs appearing in published articles by C. P. Berkey¹⁵ and C. R. Fettke.¹⁶ The count was made by drawing on the photomicrograph four diameters at 45° from each other and measuring to the nearest millimeter the dimension of each grain intersected by each diameter at

¹⁵ C. P. Berkey: N. Y. State Museum *Bull.* No. 225-6, 62-63.

¹⁶ C. R. Fettke: *Annals of the N. Y. Acad. Sci.* (1914) **23**, 193-290.

the intersection. From these data, tables (6, 7, 8, 9, 10 and 11) were constructed on which the various columns d , f , d^2 , fd^2 , fd^3 represent respectively the diameter of grain, frequency corresponding to that diameter, area per grain, area for corresponding frequency, and area for corresponding frequency multiplied by diameter. This is the correct procedure, for, if it is considered that the thin section examined is a true measure of the grain size of the rock under investigation, it is at the same time implicitly assumed that the grains all have the same height, that is the thickness of the slide, or that only two dimensions of the grain breadth and length, enter into the problem. This is true only as long as the grains are coarse enough to occur not over one grain deep in the slide; for the rock under investigation the grain diameters are amply larger than the thickness of the slide; it is therefore possible to leave out of consideration the third dimension without danger of introducing an error.

As contrasted with the computation of average size from a count made in a thin section, it is necessary, when averaging a dimensioned count of grains disseminated on a slide, to take stock of the three dimensions of the grains. The average size will be obtained by $\frac{\sum fd^4}{\sum fd^3}$ instead of

TABLE 6.—Count No. 1: Plate 12, Fig. 13, *Fettke Report*

d	f	d^2	fd^2	fd^3
1	42	1	42	42
2	23	4	92	184
3	5	9	45	135
4	4	16	64	216
5	4	25	100	500
6	2	36	72	384
7	1	49	49	343
8	1	64	64	512
9	1	81	81	728
10	2	200	200	2000
			728	4316

$$\text{Average size} = \frac{4316}{728} : 22.5 = 0.26 \text{ mm.}$$

TABLE 7.—*Count No. 2: Plate 13, Fig. 1, Fettke Reports*

<i>d</i>	<i>f</i>	<i>d</i> ²	<i>fd</i> ²	<i>fd</i> ³
1	4	1	4	4
2	11	4	44	88
3	7	9	63	189
4	5	16	80	320
5	3	25	75	375
6	3	36	108	648
7	2	49	98	686
8	2	64	128	1,008
9	2	81	162	1,458
10		100		
11	1	121	121	1,331
12	2	144	288	3,456
13	1	169	169	2,197
14	1	196	196	2,544
			1,537	14,304

$$\text{Average size} = \frac{14,304}{1537} \div 22.5 = 0.41 \text{ mm.}$$

TABLE 8.—*Count No. 3: Plate 13, Fig. 2, Fettke Report*

<i>d</i>	<i>f</i>	<i>d</i> ²	<i>fd</i> ²	<i>fd</i> ³
1	11	1	11	11
2	15	4	60	120
3	15	9	135	405
4	9	16	144	576
5	5	25	125	625
6		36		
7	2	49	98	686
8	1	64	64	512
9	2	81	162	1458
10	1	100	100	1000
			899	5393

$$\text{Average size} = \frac{5393}{899} \div 22.5 = 0.27 \text{ mm.}$$

TABLE 9.—*Count No. 4: Plate 13, Fig. 3, Fettke Report*

<i>d</i>	<i>f</i>	<i>d</i> ²	<i>fd</i> ²	<i>fd</i> ³
1	92	1	92	92
2	30	4	120	240
3	7	9	63	189
4	2	16	32	128
5	2	25	50	250
			357	899

$$\text{Average diameter} = \frac{899}{357} \div 22.5 = 0.124 \text{ mm.}$$

TABLE 10.—*Count No. 1: Berkey Report*

d	f	d^2	fd^2	$d^3 \cdot d$
1	20	1	20	20
2	26	4	104	210
3	10	9	90	270
4	8	16	128	510
5	3	25	75	380
6	6	36	196	1,180
7	5	49	245	1,750
8	4	64	256	2,040
9	1	81	81	730
10	1	100	100	1,000
11	1	121	121	1,330
12	1	144	144	1,720
13	0			
14	1	196	196	2,560
15	1	225	225	3,370
16	0			
17	1	289	289	4,930
			2,270	22,000

Average size $\cdot 22,000 \cdot 2270 = 9.7$ or, reduced to usual scale $\cdot 9.7 \div 30 = 0.32$ mm.

TABLE 11.—*Average Size*

INDIVIDUAL AVERAGE SIZE, MM.	DEVIATION	(DEVIATION) ²
0.32	0.05	0.0025
0.26	0.01	0.0001
0.27	0.00	
0.41	0.14	0.0196
0.12	0.15	0.0225
1.38		0.0447 $\div 5 = 0.0089$

Mean average size = 0.276 ± 0.065 mm.

Standard deviation = 0.095 mm.

The average size obtained microscopically is 0.276 ± 0.065 ; that obtained by crushing 0.27 ± 0.013 , an agreement well beyond dispute. It is therefore permissible to conclude that:

1. The maximum height of the curve representing the difference between the schist and the quartz plots corresponds to the average grain-size of the rock.

2. A larger percentage of rock breaks at the average grain-size or to a size in the neighborhood of the average size in the case of a heterogeneous rock than in the case of a rock presenting no weaknesses at the grain boundaries.

3. The average grain-size of a nonhomogeneous rock can be determined by a simple crushing test on sized feed.

Variation in the intensity and range of this preferential action with the relative strength of grains and grain boundaries and the range of size of grains in the rock should be expected. Manhattan schist, for instance, is very variable, and more micaceous varieties which are coarser grained should exhibit preferential breaking at a coarser range of sizes than other

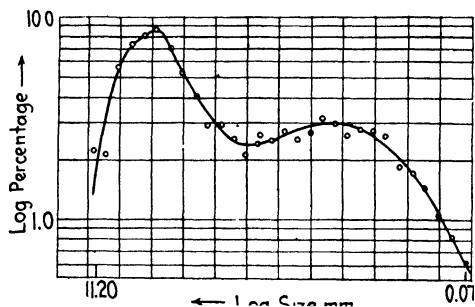


FIG. 80.—FEED, THROUGH 22.43 MM. AND ON 18.85 MM. (MANHATTAN SCHIST, SELECTED GRAINS, COARSE MICACEOUS PHASE; ROLLS SET AT 5.613 MM.)

varieties which are finer grained. This is shown well by Figs. 80, 81 and 82 which were obtained from the screen analysis of the crushed products of three groups of -22.43 $+18.85$ -mm. hand-picked pieces of schist fed to rolls set at 5.613 mm.

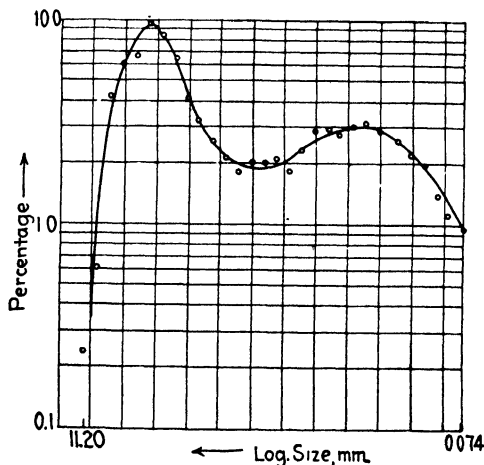


FIG. 81.—FEED, THROUGH 22.43 MM. AND ON 18.85 MM. (MANHATTAN SCHIST, SELECTED GRAINS, GNEISSIC PHASE; ROLLS SET AT 5.613 MM.)

It should further be noted that the height of the humps has been increased by selection; this agrees with the expectation that the range in grain size should be less with pieces which are more nearly alike than when very dissimilar pieces occur simultaneously.

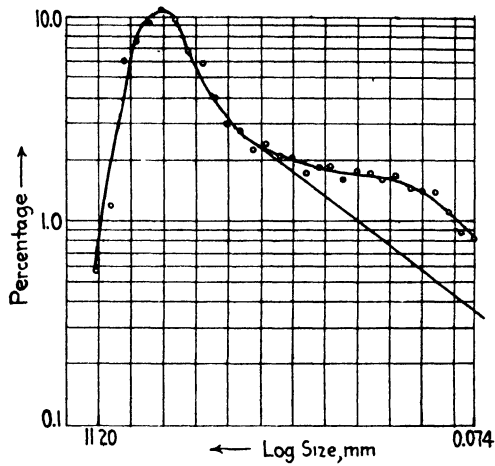


FIG. 82.—FEED THROUGH 22.43 MM. AND ON 18.85 MM. (MANHATTAN SCHIST, SELECTED GRAINS, COARSE, LUMPY, MICA-SCHIST PHASE; ROLLS SET AT 5.613 MM.)

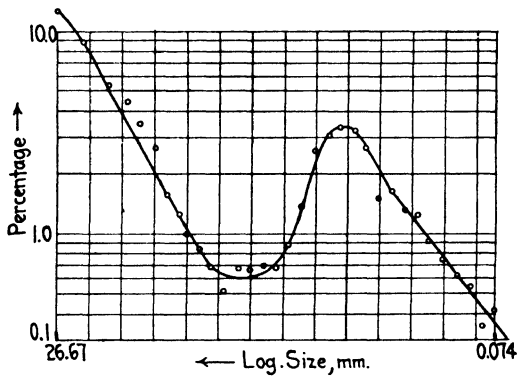


FIG. 83.—FEED ON 3 IN. AND THROUGH 6 IN. (INWOOD LIMESTONE TO DODGE BREAKER.)

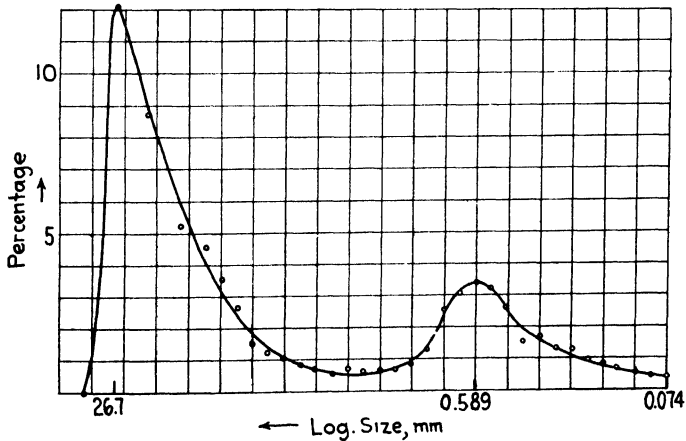


FIG. 84.—FEED ON 3 IN. AND THROUGH 6 IN. (INWOOD LIMESTONE TO DODGE BREAKER.)

Inwood Limestone

When slightly weathered, Inwood limestone is very friable. Results obtained by crushing a sample of this rock in a Dodge jaw crusher are given in Figs. 83 and 84. The hump shown by the diagram of the crushed product is more marked in this case than in the case of Manhattan schist.

Résumé

When the logarithmic size-curve of a crushed product obtained from sized feed is not a straight-line the rock is heterogeneous in character under conditions that yield a straight line in the fine range with quartz as feed.

The position of the hump in the curve indicates the size to which the rock breaks in preference. The height of the curve is in a way a measure of the intensity of this preferential action.

ACKNOWLEDGMENTS

The author wishes to thank Prof. Arthur F. Taggart for his valued suggestions and discussion, Mr. R. T. Bergman for collaboration in the tests run with the Abbé mills, Prof. J. J. Galloway for communication of data on wear tests, and Mr. G. E. Bock for his review of the manuscript and suggestions. The experimental work was done in the laboratories at Columbia University.

DISCUSSION

J. B. PORTER, Montreal, Que.—Mr. Gaudin is absolutely right in his statement that we must size carefully in some way or other, stuff under 200 mesh, if we are to get any light upon the laws of crushing. Although these laws of crushing may seem very theoretical, they will, when satisfactorily worked out, be of great assistance in practical crushing.

I have had exactly the same experience that Mr. Gaudin refers to in his statement that there are two classes of rock; that is, the homogeneous and the heterogeneous rocks. For our main crushing experiments at McGill University, we have been using a uniform type of rock for the last 10 to 15 years, namely a basic igneous tinguaitite rock, which is of very uniform hardness and strength.

Recently, in carrying out some sizing tests, we first crushed the rock through rolls and then sized and resized it into a series of grades according to the square root of two sieves and in the finer sizes to the square root of four. Each lot of this was sieved and resieved, until we got it almost absolutely free from undersize, and then we determined the efficiency of our sieves when working upon charges at varying weights and sizes.

With our tinguaita we found a very interesting result. The graph of efficiency of sieving showed a series of waves. That is to say, the rock would easily sieve say through the 10 to 14-mesh, and we would get an efficiency in 1 min., sieving under standard conditions, of 80 to 90 per cent. of the total undersize. That amount of that particular grade would go through, but with another grade, let us say, 40 mesh, we would find that instead of the efficiency being 80 to 90 per cent., we would only get about 15 to 20 per cent. through in the standard time although all of it would go through ultimately. In the next size larger than that, we would get up to 60 and 70 per cent. through in the same length of test. Then again when on still finer stuff we got another drop and so on.

In brief, although the rock was graded according to a fixed ratio from a relatively coarse mesh down to excessively fine, certain portions of it were very difficult to size through their proper grades of sieves, whereas the next grade or two above and below would be very much easier to get through. So the curve went in a series of waves in the range between 10 mesh and 200 mesh, two or three high points and intermediate low points.

We have another but very different type of rock that gave a smooth curve, of increasing difficulty as it became finer, but quite different from the tinguaita that gave the wavy line, and our experiments generally speaking, support Mr. Gaudin's contention and also indicate that you must modify your sieves somewhat from any uniform size ratio if you want to get anything like equal portions or equal ease of sieving in successive sizes.

A. M. GAUDIN.—I want again to stress the importance of sizing —200-mesh material. I computed that if we were to picture the smallest grain of —200-mesh material as the size of a sand grain, the largest one would be the size of the Woolworth building, or somewhere near that.

C. P. McCORMACK, Cleveland, O.—Mr. Gaudin, what size do you consider in —200-mesh approaches a colloid, and what are you going to do with that in moving it for crushing?

A. M. GAUDIN.—I imagine colloids run from about one or two microns to about 0.01 or 0.1. I have graded —200-mesh material from 75 down to 5 microns. These various graded products, notwithstanding their small size, still look like sand and feel gritty to the teeth.

L. F. CLARK, New York, N. Y.—As I understand it the efficiency of this grinding operation is based, according to Mr. Gaudin, on the change in area of the various particles, taking the area of the feed against the area of the product. If we consider ball milling as a contact of points and rod milling as a contact of lines, I would like to know if one could consider the fall of the stamp as contact of surfaces? From this the

product of a single impact could be obtained that would be a simpler point of attack from which to figure efficiency of crushing. That is to say, the action in a ball or rod mill is very complicated, whereas in a stamp it would be very much simpler, and it would seem to me that the product of a single fall of a stamp would furnish a measurable action for calculating the efficiency where a definite single energy impact would also be known.

A. M. GAUDIN.—I believe with Mr. Clark, that the crushing action in practical stamp milling may be considered as caused by a contact of surfaces, but I do not think this makes the ordinary stamp mill a theoretically simpler crushing unit. Most crushing machines present a sizing action of one kind or another. The jaw crusher, for instance, has a sizing action on particles larger than the set of the jaws. The gyratory crusher also exerts a sizing action on particles larger than the set of the crusher. In a rod mill, large particles keep small particles from being crushed, which is not the case to the same extent with a ball mill. The proof lies in the fact that although the curvature of a 1-in. rod is the same as that of a 1-in. ball, yet the 1-in. rods will nip particles of a size that 1-in. balls cannot nip. The reason for that is that the rods will break particles without coming in contact, whereas the balls apparently have to come in actual contact. This indicates that there is a single action in a rod mill. In a stamp mill, there are several sizing actions: One is due to the stamp coming down on the shoe; another to the water which removes the fines; and still another to the screen. The existence of these numerous sizing actions makes the action of crushing by stamping a more complicated problem rather than a simpler one as compared with the action of crushing in a ball mill.

Further advantages of a ball mill as compared with a stamp mill are ease of operation and the possibility of operating on a comparatively small unit.

On the other hand, carefully conducted tests with single-drop stamps, in which the height of drop and amount of material was under control, would seem to be an excellent point of attack to determine crushing efficiency. Such tests, however, would have the disadvantage of being still further removed from practice than batch-ball-mill or batch-rod-mill tests would.

J. H. LEWIS, Berkeley, Calif.—I should like to know the formula for spring tension of the rolls under operation.

A. F. TAGGART, New York, N. Y.—It is my observation that the usual method of determining operating spring tensions is to make them as great as possible without breaking the roll. The general tendency is to tighten until something goes wrong, then the operator decides that the springs cannot be tightened that much. Generally, the tighter the

springs the more crushing is done at one passage of material. The only loose-spring, high-capacity practice that I know is in some of the large copper mills where rolls are choked with an enormous closed circuit.

J. H. LEWIS.—They are operating at the closed circuit more than they used to; the spring tension is very much lower than it used to be.

Another question I would like to discuss is: In ball-mill operation in open-circuit work, it is usually necessary to have a certain amount of fines in with the feed; that is, the ultimate production of crushing will be greater with a certain amount of fines in the feed than with no fines whatever. That seems to contradict Mr. Gaudin's statement relative to washing out the slimes as fast as they were reduced.

B. R. BATES, New York, N. Y.—May it not mean that a certain amount of fines that will stick to the grinding material is required? If you have enough fines to make up a pulp that will stick to those surfaces, when they fall, they do the crushing; whereas if they are perfectly clean, your product all more or less is down at the bottom—it is not being crushed between the falling balls.

J. H. LEWIS.—In other words, the fine slime in the mass of feed has the effect of keeping the largest particles more mixed in the mass of balls, is that it?

B. R. BATES.—I think so. That was brought out in work done at the plant of the Utah Copper Co. If you remove all the slimes, the capacity of the mill diminishes. It is necessary to have a certain amount of fines that will give a pulp.

A. F. TAGGART.—The apparent liquidity of a pulp that is made up of water and sized particles is very different, as you know, from the apparent liquidity of a pulp containing the same amount moisture but with fine material in it. The fine material makes the pulp viscous and thereby makes it disperse through the mass of crushing media. This is the explanation for the higher capacities on feeds containing some slime.

J. A. BAKER, Newfield, N. J.—Some small-scale experiments which we have made by adding a certain percentage of slimes to the suspension of sand and grinding it, did not support the contention that the slimes assisted the bearing of it, but it brought out the fact that a very small variation in dilution made a very large difference in the crushing efficiency. That point should be considered also before arriving at a final decision.

If you had a certain critical density, did a move either side of that density result in a decrease of grinding?

J. A. BAKER.—It did.

A. F. TAGGART.—What was the critical density?

J. A. BAKER.—I cannot give you the figure offhand, but it is a matter of record.

A. F. TAGGART.—What was the effect in the mill when you exceeded the critical density? Did you get difficulty in discharge?

J. A. BAKER.—The experiment was performed on the batch basis.

C. J. GUNDEROTH, Milwaukee, Wis.—Have you ever heard of rolls built with a hydraulic resistance to take the place of springs?

J. A. LEWIS.—There is a manufacturing concern that is experimenting on hydraulic resistance in place of springs.

C. P. McCORMACK.—In grinding —200-mesh material to —450 mesh, would it be necessary to size below 200 mesh to get the best efficiency?

A. M. GAUDIN.—I think, if it holds true that classification in closed circuit with grinding is desirable at 200 mesh, that the same would hold true to around 400 mesh.

Mr. Baker, with reference to the tests that you mentioned in which you investigated the effect of dilution on wet-crushing efficiency, was dilution the only variable in the tests named?

J. A. BAKER.—The dilution was the only variable in one series of tests, and the amount of slime was the other variable.

A. M. GAUDIN.—In the tests where the dilution was the only variable, how did efficiency vary with dilution, in the range of 25 to 50 per cent. of dilution?

J. A. BAKER.—We did not cover so wide a range. We were working around 25 per cent. moisture, probably 30 to 35, and our test brought out that that dilution was very critical, that ordinarily around 30 to 45 per cent. dilution was suitable for a tube mill, that in a fine mill you might find about 30 to 35 per cent. dilution.

A. M. GAUDIN.—What were the efficiencies?

G. M. DARBY, Westport, Conn.—The efficiency dropped off more rapidly as you went up in the dilution.

A. M. GAUDIN.—Which might indicate that at around 15 or 20 per cent. dilution, you would have higher efficiencies, would it not?

G. M. DARBY.—We concluded that you might bring up the dilution as you increased the number of small particles.

B. R. BATES.—The dilution would depend considerably upon the characteristics of the material. If you were on Witwatersrand ore, which has a very small amount of what we normally call slimes or colloidal material, it would probably require less dilution than if you were working on a slimy ore such as we have in Mexico. The object would be to get a

certain viscosity of pulp within your tube mill; one that would stick to the balls.

A. F. TAGGART.—If you work from below the capacity of the mill, the results when the dilution is changed are not at all distinctive. We did some work recently in the laboratory at Columbia—a student run—in which three distinctly different dilutions were given in the instructions, in operating a rod mill, and the screen tests checked so closely that they might have been duplicate tests on the same sample, rather than screen tests taken for three different samples. We were feeding under capacity for the mill in each particular run. In other work, when the mill was being fed up to capacity in each case and when it was being operated to produce a given character of overflow or a given character of discharge, the changes in dilution were noticeable.

A. M. GAUDIN.—The tests mentioned by Prof. Taggart, were made with Manhattan schist, a heterogeneous rock, most of the material produced being broken at the size of preferential breaking, which effect may very well have masked some influence of dilution that might be better shown with a homogeneous rock.

C. E. LOCKE, Cambridge, Mass.—The author subscribes to the theory having to do with the angle of nip of rods in the rod mill. This theory appeared about a year or more ago, and I was unable in my own mind to accept it fully. It seemed to me that the rods in a rod mill were not exactly similar to rolls in that rolls are set a definite distance apart and must necessarily nip the particles in order to effect a crushing, whereas the main crushing action of rods could form actual movement of rods relative to one another. At one instant two rods may be receding from one another and the space between them becomes occupied by ore. Later, these two rods approach one another and the ore is crushed by direct pressure. In this case the only application of the nip theory is in determining how far the zone of crushing will extend each side of the center line joining the axes of the two rods. In other words, a particle on the center line will be crushed, no matter how big it is, but particles off the center line will be held and crushed if their angle of nip is small or will be forced out and remain intact if their angle of nip is large.

I take it that you do not describe similarity between rod-mill and roll-mill angles of nip.

A. M. GAUDIN.—In tests performed with experimental rod mills at Columbia, the coefficient of friction would have to be about 0.9 if it is assumed that the rods came together. I believe the extreme values for the coefficient of friction as given are 0.3 and 0.7. The conclusion is then that the rods do not actually come in contact but are kept apart by grains of rock. Another reason to discard the possibility of a coefficient of friction of 0.9 in rod milling is gained by experience with ball

milling in which I have shown that the maximum coefficient of friction is about 0.4.

C. E. LOCKE.—Is it not true that there is the possibility of the same action in the rod mill as we get with the jaws, which would account for that high angle of nip which you computed? .

A. M. GAUDIN.—I believe that there is a possibility of the action in a rod mill being similar to that obtained in a jaw crusher, but such an action does not differ much from the crushing action in rolls.

L. T. WORK, New York, N. Y.—Has Mr. Gaudin any particular method of sizing microscopically as compared with the sieve method? That difference in the sizing has to be correlated.

A. M. GAUDIN.—No matter how large the difference will be between microscopic and other methods of sizing they will always be insignificant in comparison with the differences in size between, let us say 200-mesh grain and 5-micron particles, 5 micron and 0.1 micron particles, etc. So that although it is important to keep in mind the existence of difference there, they should not be overestimated. In a few cases I have made comparative sizing tests by microscope and settling. I have found some differences between these: The microscope will generally show coarser —200-mesh material than settling because particles will lie flat on the slide so as to show the two largest dimensions, and the two largest dimensions are not the controlling dimensions in determining settling velocities.

L. T. WORK.—In some of my own experimental work and in the work of the Bureau of Standards, it was found that when a particle is lying flat, it has its two larger dimensions visible in the microscope, and that the shorter dimension is equivalent to the diagonal of a 200-mesh screen. This sometimes helps in correlating the difference between the microscopical sizing and the screen sizing.

R. H. RICHARDS, Cambridge, Mass.—I have always considered that if you had length, breadth and thickness, the length being the greatest and the thickness the least, that if you took the width and called that the size of the grading, you came about as near as any basis upon which you could work.

Chloridizing Mill of the Standard Reduction Co.

BY H. P. ALLEN* AND WM. C. MADGE,† SALT LAKE CITY, UTAH

(Salt Lake City Meeting, September, 1925)

THE chloridizing mill of the Standard Reduction Co. is located about 75 miles south of Salt Lake City on the Tintic branch of the Denver & Rio Grande Western R. R. and 12 miles from the Tintic Standard mine. The daily capacity is 200 tons of a siliceous, low-grade, silver-lead ore from this property. It has operated continuously since it was started in January, 1921.

The process consists essentially of a chloridizing roast followed by a percolating leach with a nearly saturated solution of common salt, acidified with sulfuric acid, the precipitation of silver on sponge copper and of copper and lead on tin-plate cuttings. The precipitates are shipped to a smelter. Some of the general ideas involved are said to have been used by Augustin in England, in 1840. A number of textbooks treat of the subject, especially the chloridizing roast followed by a leach with sodium hyposulfite or amalgamation. The process was revived in this district by Theo. P. Holt, N. C. Christensen, the Bureau of Mines, and others.

NATURE OF ORE TREATED

The average assay of the ore treated during 1924 is as follows:

Gold, ounces per ton.....	0.025
Silver, ounces per ton.....	18.26
Copper, per cent.....	0.30
Lead, per cent.....	5.00
Silica, per cent.....	65.00
Iron, per cent.....	10.00
Lime, per cent.....	0.70
Sulfur, per cent.....	3.00
Arsenic, per cent.....	0.70

The silver is finely disseminated and occurs as native, combined as a sulfide and, to a very small extent, as the chloride. The lead may be present as carbonate, sulfide, or sulfate.

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PREPARATION OF ORE FOR ROASTING

The ore is received in standard, bottom-dump, railroad cars, crushed to 3 in. by a Kennedy 6F gyratory, then to $\frac{3}{4}$ in. by a 36-in. horizontal Symons disk. Finally the ore, with 8 per cent. salt, is run through two sets of Allis-Chalmers rolls, 16 by 48 in., working in series and in closed circuit; the final product passes through an 8-mesh screen with a clear opening of 0.071 in. Three Mitchell and two Colorado impacts are used in the roll circuit. The results of a screen test on the roll product and the distribution of the metals are as follows:

SCREEN ANALYSIS	PER CENT.	SILVER, OUNCE	COPPER, PER CENT.	LEAD, PER CENT.
On 10 mesh.....	0.1	19.6	0.19	3.1
Through 10, on 20....	24.1	20.6	0.29	3.8
20, on 30.....	24.5	18.2	0.49	4.4
30, on 40.....	7.2	17.6	0.29	4.3
40, on 50.....	7.8	19.4	0.29	4.5
50, on 60.....	2.4	19.3	0.39	5.1
60, on 80.....	6.6	21.4	0.39	5.7
80, on 100.....	3.4	24.6	0.49	7.5
100.....	23.9			

After grinding, the ore-salt mix is sampled by a mechanical sampling device in batches of 70 tons, each batch being run to a separate bin. For the purpose of furnace control, the sample is tested for its reducing power on litharge, which test indicates its fuel value. The latter is then adjusted to suit the requirements of the subsequent roasting operation by the addition of coal dust; this usually amounts to between 1 and 2 per cent. Before passing to the bins over the roasters, the mix is moistened with just enough water so that it will stick together as a ball when pressed in the hand. The actual amount of water needed will vary according to the fineness of the ore, but is approximately 7 per cent.; the ore, as received at the mill, has a moisture content of 2 to 3 per cent. The mix is now ready for the roasters.

ORE ROASTED IN HOLT-DERN FURNACES

There are nine Holt-Dern blast roasters. These consist essentially of a row of reenforced-concrete boxes 7 by 9 by 5 ft. deep inside, set end to end; on the bottom are mechanically operated grates with hoppers underneath. On the long side, and 30 in. above the grates, are two double work doors which run the full length of each furnace. Above the furnace are the charge bins, with four segmental gates for each furnace. Leading into the hopper under the grates is a pipe through which an air blast is supplied at 8 oz. pressure by a direct-connected Sturtevant fan. A common flue, through which the gases are drawn, runs the full length of the furnaces.

These furnaces are operated as follows. Starting with a bed of hot calcines, about 10 in. deep, on the grates, sufficient ore mix is let down from the bins to fill the furnace even with the bottom of the work doors. After leveling, by hand, the air gate is opened and the sulfur and coal in the charge, ignited by the hot calcines on the bottom, gradually burn upwards, and as a rule, quite evenly over the whole area of the furnace. This takes a little over 3 hr.; at the end of this time, the whole mass is at a dull red heat, or about 700° C. The air gate is then closed and the grates put into motion so that the charge is shaken into the hopper below, leaving enough hot calcines on the grates to ignite the next charge. The operation is then repeated. With each "drop," $4\frac{1}{4}$ tons of calcines are obtained or 25 tons per furnace per 24 hr.

LEACHED BY PERCOLATION

As soon as convenient after shaking the calcines from the roasters, the gates at the bottom of the hoppers are opened and the calcines run into a concrete launder through which a stream of brine is flowing. This flushes the calcines into one of six concrete leaching tanks. These tanks are 28 ft. in diameter by 11 ft. deep, inside, and have a filter bottom, made up of crushed quartzite and two 3-in. earthenware cocks for discharge. A tank will hold about 225 tons of calcines when filled to within 8 or 10 in. of the top. After leveling, leaching is commenced. The effluent liquor is received in two concrete sump tanks of the same size as the leaching tanks. The first, and richer, part of the solution is received in one of these and is designated "pregnant solution." It ordinarily carries about 3 oz. per ton of silver and 14 lb. of lead. The subsequent solution is received in the second tank and is called "weak." This weak solution is used for sluicing the calcines from the roasters and for the first 24 to 48 hr. of the leaching period. After precipitating the metals from the pregnant solution, a barren liquor is obtained; this is used as the second leach solution over the next 48 hr. period, being received in the weak sump after passing through the leaching tank. Finally, each tank is washed for 8 hr. with water, to replace the last solution, then drained and sluiced through two bottom gates to the sump.

SUMMARY OF LEACHING CYCLE

	Hours
Sluicing from roasters to leaching tanks with weak solution.....	24
Weak leach.....	48
Barren leach.....	48
Water wash.....	8
Draining.....	2
Sluicing tails to dump.....	8

The amount of solution that will run through a tank of calcines in 24 hr. varies from 200 to 300 tons.

PRECIPITATION ON SPONGE COPPER AND SCRAP IRON

The pregnant solution is pumped by air lifts from the sump tank to the silver precipitator. This really amounts to a four-compartment Pachuca tank with an air lift in each compartment for agitation. Each compartment is 11 ft. 4 in. by 11 ft. 4 in. in cross-section and 10 ft. deep, to a pyramidal bottom, which adds 8 ft. to the over-all depth. It is built of reenforced concrete. In this, the solution is agitated with sponge copper to precipitate the silver, and flows through the four compartments in series: the fine copper is added intermittently as needed. When a sufficient amount of silver has accumulated in the first compartment, the solution is bypassed; that remaining in the compartment is decanted and the precipitated silver run to a filter box. Before shipping, this material is treated as noted later.

The effluent from the silver precipitator runs to eight concrete boxes, varying in depth from 18 in. to 3 ft., by 5 ft. wide and 30 ft. long, and filled with tin-plate cuttings. The boxes are provided with wooden grids, on which the cuttings rest, and with four baffles to interrupt the flow. Additional scrap is put in every day and one box is thoroughly cleaned each day, the precipitated copper being washed to a settling box. Part of this is used as the precipitant of the silver; the remainder is shipped to the smelter. It will contain about 100 oz. of silver per ton and 50 per cent. copper.

The solution flowing from the eight copper boxes is pumped with an "Olivite" centrifugal to a rectangular concrete tank containing about 1260 ft. of 1¼-in. copper pipe through which low-pressure steam is passed. Thus the solution is brought to a temperature of 75° C. and is then passed through fifteen additional boxes, similar to the copper boxes and likewise filled with tin-plate cuttings. In these, the lead is precipitated. It is necessary to add live steam also to these boxes, to maintain the temperature. The boxes are kept as full as possible with the cuttings and two of them are cleaned each day, the cuttings being removed and washed and the lead sluiced to a drain box; this is shipped to the smelter without drying. A partial analysis is given below:

Gold, oz.....	0.005	Alumina, per cent.....	3.00
Silver, oz.....	6.58	Zinc, per cent..	0.50
Lead, per cent.....	70.27	Arsenic, per cent.....	0.10
Copper, per cent.....	5.12	Antimony, per cent.....	0.10
Insoluble, per cent.....	1.70	Bismuth.....	trace
Iron, per cent.....	5.52	Tin.....	trace

Moisture content as shipped 21.38 per cent.

When using tin-plate cuttings, it has been found advantageous to remove first the tin coating; this is accomplished by treating them with a solution of caustic soda containing a small amount of litharge. The following reaction is involved.



The lead oxide is obtained by simply heating the lead precipitate in contact with air. The bales of scrap are loosened, placed in shallow iron boxes, and the caustic solution circulated through it, having in the circuit a small steam coil for heating. The tin at present is not recovered. The method is outlined in Schnabel, Vol. 2, page 541.

ADDITIONAL TREATMENT GIVEN SILVER PRECIPITATES BEFORE SHIPMENT

The precipitate, as taken from the silver precipitator, will run 30 per cent. silver (8750 oz.), 15 per cent. copper, 2 per cent. lead, 25 per cent. arsenic, and 1 to 2 per cent. antimony, the remainder being largely insoluble, iron, and alumina. After washing and draining, this is placed on a small reverberatory hearth and heated slowly with an oil flame to dry. The temperature is then increased somewhat, when about 60 per cent. of the arsenic will be volatilized, the fume being caught in small bags. When the fumes are no longer emitted, the material is brought to a dull red heat and the copper oxidized. The product is then removed from the furnace, the lumps broken, and leached with a hot 25 per cent. sulfuric acid solution; this reduces the copper to about 1 per cent. and the arsenic to less than 0.75 per cent. Finally it is dried, sacked, and shipped, by express, to the smelter. It will run from 10,000 to 14,000 oz. silver per ton.

RECOVERIES AND COSTS

The recoveries of both silver and lead have gradually improved and, at present, the following can be consistently obtained. Gold none; silver, 89.8 per cent.; lead, 65.7 per cent.; copper, 52.2 per cent.

The following cost data represent the average for the year, 1924.

COST OF MILL TREATMENT PER DRY TON

Dept.	1	2	3	4	5	6	7	8	Total
Operating labor	\$0.238	\$0.244	\$0.334	\$0.109	\$0.312	\$0.113	\$0.233	\$0.110	\$1.738
Operating supplies	0.071	0.510*	0.192	0.112	0.321	0.065	0.040	0.008	1.319
Repair labor	0.099	0.130	0.181	0.019	0.053	0.004	0.067	0.553
Repair supplies	0.175	0.174	0.099	0.013	0.028	0.006	0.044		0.539
Power	0.086	0.090	0.084	0.005	0.007	0.002	0.009		0.283
Total714	1.148	0.890	0.258	0.721	0.190	0.393	0.118	4.432

* Includes the cost of all salt.

Department 1, unloading, crushing and grinding; 2, roasting; 3, leaching and precipitating silver and copper; 4, silver-product treatment; 5, lead precipitation; 6, chemical laboratory; 7, undistributed; 8, office and supervision.

Average labor wage per 8 hr. day	\$ 5.00
Salt costs, f.o.b. mill, per ton	4.00
Slack coal, f.o.b. mill, per ton	3.05
Tin-plate cuttings, f.o.b. mill, per ton	18.00

The cost of all experimental work to improve recoveries or operation is included in the above.

MISCELLANEOUS OBSERVATIONS

Roasting

Probably the roasting operation is the most satisfactory step in the process, whereas formerly roasting apparently caused much trouble on account of the volatilization of the silver and the skill required to obtain good chloridization. Using this method, with a reasonable amount of attention, there is only a negligible silver volatilization loss and a good conversion usually results. While it is an intermittent operation, two men per 8-hr. shift will roast 75 tons of ore and have time to spare.

As in most furnace operations, some points must be carefully watched, especially those regarding the preparation of the mix. While 8 to 10 per cent. of salt is used, a satisfactory chloridization may be obtained in the furnace with 5 to 6 per cent.; the balance is used to maintain a high chlorine concentration in the leaching solution. No detrimental effect has been observed when using this large excess, unless it is when the furnaces are running a little hot; then the salt may fuse, making the calcines slightly more difficult to shake through the grates. A thorough mixing of the salt is essential. The salt used is commonly known as "smelter salt" and is obtained from the Morton Salt Co. at Burmeister, Utah. It is shipped in bulk in bottom-dump cars and is handled the same as ore. In size, the crystals vary up to possibly $\frac{1}{2}$ in. Salt containing a large proportion of fines, or "dairy salt," is more difficult to pass through the plant, as it hangs up in all the bins. The salt, as received, is quite pure, samples usually showing a chlorine content equivalent to 97 per cent. NaCl.

It has been found in blast-roasting Tintic Standard ore, that for the most favorable operating conditions the sulfur permissible in the mix must be between 2 and 4 per cent. Good chemical results have been obtained with 1 per cent. sulfur, the balance of the fuel necessary being made up with fine coal; but the tendency on low-sulfur charges is toward uneven burning and a rapid loss of heat during the recharging period. Above 4 per cent. sulfur, Standard ore fuses too easily so that the resulting calcines are caked or sintered in hard lumps, which require a long time to shake through the grates. It is not the additional sulfur in itself that causes the fusion but the fusion point of the whole charge is lowered by the addition of the sulfide ore. With a high-sulfur charge, when the rate of burning is decreased by decreasing the air supply, the fusion still takes place.

The sulfur content is determined by fusion with litharge; this is supposed to be the sulfide sulfur but, of course, any other material that

will reduce litharge will be reported as sulfur. It is the heating value of the charge that is sought. Some idea of the requirements in the charge may be obtained by noting that with a 3 per cent. sulfur $1\frac{1}{2}$ per cent. coal is used; and as the sulfur changes, the coal is varied using the ratio sulfur: coal = 1:0.65. This method of adjusting the fuel value is purely empirical but commercially uniform results are obtained. It would be desirable to have a calorimeter determination on the roaster charge, but this is difficult for the total heat value is so low that an undue portion of some substance with a high heat value must be added in order to get the calorimeter charge to burn. However, some good work along this line has been done by the Salt Lake station of the Bureau of Mines and it is quite possible that a more satisfactory method for furnace control will be worked out.

The quantity of water in the mix is important. Water is added primarily for the purpose of agglomeration and so forming a more porous orebed. It is supposed to assist in the chloridization, also, by the formation of hydrochloric acid. Too much water makes a hard calcine; too little makes slow roasters with a tendency to be "spotty." If the ore just sticks together when pressed in the hand it is about right. This is another unscientific procedure but moisture determinations are useless; 7 per cent. water is close to the amount usually needed with the present size of ore feed.

It would probably be difficult, surely slower, to blast-roast the ore if ground finer than it now is although no work has been done with increased blast pressure.

It does not require a great deal of skill to operate the roasters properly but the results obtained are largely dependent on the conscientiousness of the firemen. The roaster should be "dropped" immediately the operation is completed, thus the heat in the charge is conserved and a good ignition obtained on the next round; also, the calcines remaining on the grates should be leveled and care taken that there are hot calcines over the whole earth area. Spots that are a little cold should be covered with hot calcines from one of the other furnaces, or the next charge will develop dead spots, which must then be shoveled out or poor results obtained.

Leaching

Presumably, the silver has been converted to the chloride or sulfate in the roasters. (About half of it is soluble in strong ammonium hydroxide.) A strong brine is used for leaching but after having made the round trip through the plant a few times, it contains small amount of many substances. A number of determinations are made every day on the pregnant solution, the following being an example.

Specific gravity	1.24 to 1.30
Acid, lb. per ton expressed as H_2SO_4	2 to 5
Silver, oz., per ton	3 to 5
Lead, per cent. (10 to 30 lb. per ton)	0.5 to 1.5
Copper, per cent.	0.1
Chlorine, per cent.	12 to 15
Sulfur, per cent.	0.75 to 1.2
Iron, per cent.	1 to 2

The amount of "ic" salts in solution is so small as to be almost indeterminable, the solution oxidizing very slowly in contact with air. This is unfortunate as the higher oxidized forms of both iron and copper, when dissolved in the brine solution, are good solvents for metallic silver and the sulfide, should these chance to escape the action of the roasters.

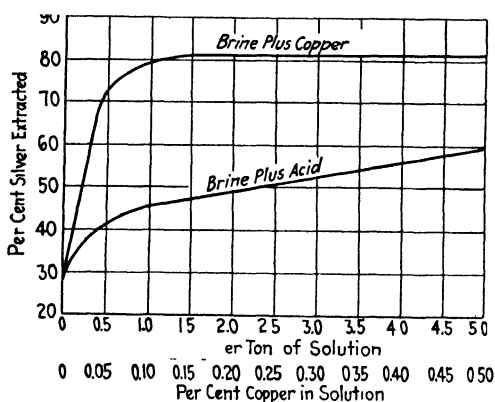


FIG. 1.

It is interesting to note the effect of the addition of very small amounts of copper sulfate to a fresh brine solution in its action on Tintic Standard ore without roasting, as shown by Fig. 1. The sample was ground to pass 120 mesh and leached by agitation, first with brine to which different amounts of copper sulfate were added and then, for the sake of comparison, a second portion with a brine carrying different amounts of sulfuric acid.

A small amount of free acid is necessary for consistent results in the solution of the silver. At times, especially when a rapid leach is made, a neutral brine dissolves the silver, but in the routine of plant leaching it is decidedly unsafe to allow the solution to approach neutrality more closely than is shown in the analysis. The silver is dissolved when using a solution short of acid and is then precipitated in the leaching tank, for while the top portion of the tailings will have a normal silver content the lower portions will steadily grow richer until they contain more than the original heads. But a small part of this silver can be dissolved when the tails are subjected to further leaching with solutions highly acidified.

Just what substances in the calcines cause this precipitation have not been determined. Lime, which exists in the ore up to 1.5 per cent. zinc, which seldom runs as high as 0.3 per cent., and metallic iron, introduced in grinding, have been investigated as possible interfering elements but no definite data obtained show that any of these could be the cause of the trouble.

The acid content of the solution is maintained for the most part by the direct addition of 66° sulfuric acid, although a small amount is absorbed by passing the solution through a spray chamber in the roaster flue system.

Iron even in the “-ous” state probably aids in the solution of the silver. Total iron seldom builds up as high as 2 per cent. in the solution in spite of the fact that all the precipitating of the metals is, in reality, done with scrap iron and no effort is made to remove it.

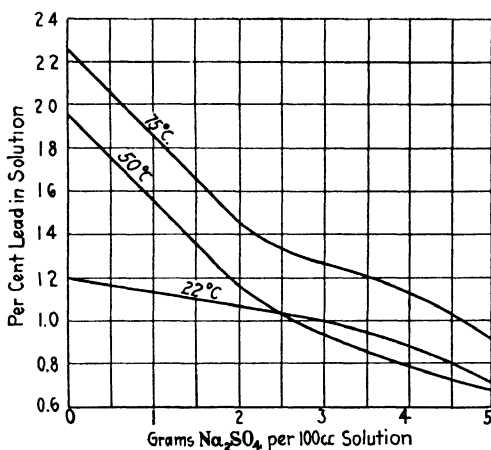


FIG. 2.

Trouble has been experienced when working with a solution saturated with respect to salt; *i. e.*, one from which salt will separate on standing a short time. Being a denser, more syruplike liquid, it percolates more slowly and it does not seem to have the dissolving power for silver that a slightly weaker solution has. This is contrary to accepted solubility data as to silver chloride in brine. More acid will not correct the trouble; in fact this difficulty is not at all times apparent. No good reason has been found as to why this is so.

The mill solutions will carry between 25 and 30 oz. of silver per ton; as this concentration is not approached in practice, the solution has ample carrying capacity for silver. Dissolving the lead, however, is quite a different problem. Nearly all of the lead in the calcines is considered as being present as the sulfate and not as the chloride. It is well known that the amount of this substance that a brine will carry is dependent on the

solution temperature, chlorine concentration, and sulfate content. The most difficult of these to control is the sulfate content and, while a number of schemes for removing this have been suggested, including freezing, evaporation, and the addition of various reagents, few have much merit commercially. By keeping the sulfate content of the leaching solutions down to 2 per cent. or under, expressed as Na_2SO_4 , it would be possible to obtain about $1\frac{1}{4}$ tons additional lead per day.

The effect of sulfates is shown in Table 1 (and graphically in Fig. 2), to obtain which, an excess of lead sulfate was left in contact with a brine solution containing 26 per cent. salt and the different amounts of sodium sulfate given, until it would dissolve no more. Also, the improvement by increased temperature is shown. It will be noted that the solutions with the large amounts of sulfate are not benefited as greatly by raising the temperature as those low in sulfates.

TABLE 1

Na_2SO_4 in Solution, Grams per 100 c.c.	Per Cent. Lead Carried by Solution after Saturation with PbSO_4		
	at 22° C.	at 50° C.	at 75° C.
none	1.20	1.96	2.23
1	1.13	1.58	1.86
2	1.07	1.15	1.45
3	1.00	0.97	1.27
4	0.84	0.79	1.13
5	0.73	0.69	0.91

Calcium chloride was long ago recommended as a precipitant for these objectionable sulfates, but 70 to 75 per cent. CaCl_2 costs \$41.90 per ton delivered to the mill and it would require at least 5 tons a day. That this reagent improves the solution as a lead solvent is shown by the following experimental data. In this case, the plant solution was treated with different amounts of the calcium chloride to obtain the varying sulfate contents indicated. Lead sulfate was left in contact with frequent stirring until the solution would no longer dissolve it.

TEST NUMBER	SO_4 IN SOLUTION, PER CENT.	LEAD DISSOLVED, PER CENT.
1	4.41	1.21
2	2.85	1.51
3	1.62	1.83
4	0.32	2.25
5	0.13	2.47
6	0.14	2.42

Slacked lime may be used in place of part of the calcium chloride, but alone it apparently acts as a precipitant for the sulfates only when there

is iron in the solution, the resultant precipitate being a basic sulfate of iron. This is a very disagreeable material to handle as it is bulky and gelatinous. Also, lime acts very slowly and requires long agitation with the liquor to obtain efficient results. Finally, it is preferable to carry iron in solution.

To discard enough solution each day to control the sulfate content has been suggested, but this had no attraction commercially as it would require some 50 tons of salt.

About the most feasible plan, probably, is to increase the number of leaching tanks, thus allowing sufficient time to pass the desired amount of solution through the calcines; then the only added operating expense would be the cost of circulating the solution. In line with this, one of the tanks was held in the mill circuit for nine days as an experiment and an extraction of 92.5 per cent. of the lead was obtained.

Precipitation

Each day 1000 tons of pregnant solution are delivered to the precipitating department and the silver precipitated first by means of the copper afterwards obtained in the iron boxes. Working in this manner, the copper is never completely replaced by the silver. When the material reaches a copper content of about 15 per cent., the remaining copper behaves as though it were coated with some protecting substance and the silver begins to dissolve. The difficulty has been attributed to arsenic which is thrown down in the metallic state in both the silver precipitator and iron boxes. The remaining copper is not soluble in weak acids.

Of the precipitation of copper on iron, little need be said as the operation is common practice. As the copper product is used in an agitating apparatus with a continuous overflow, it is desirable to have it coarse or granular so that it will not float out of the silver precipitator. Large pieces of cast scrap give a more granular precipitate than light tin plate but the latter has the advantage of increased surface and makes a reagent free from adhering foreign matter that usually accompanies ordinary scrap iron. On the other hand, where it is necessary to keep the precipitator boxes filled at all times, the cuttings are more difficult to wash.

In the precipitation of lead on iron, the solution must be maintained at a relatively high temperature in order to get a sufficiently rapid action; 75° C. secures satisfactory results with the present precipitating capacity, but the solution must come in contact with the iron and not be allowed a chance to bypass. As now conducted, the cleaning of the boxes calls for a high labor charge, but without doubt this can be greatly improved should it be decided to continue the use of tin-plate cuttings as the precipitant.

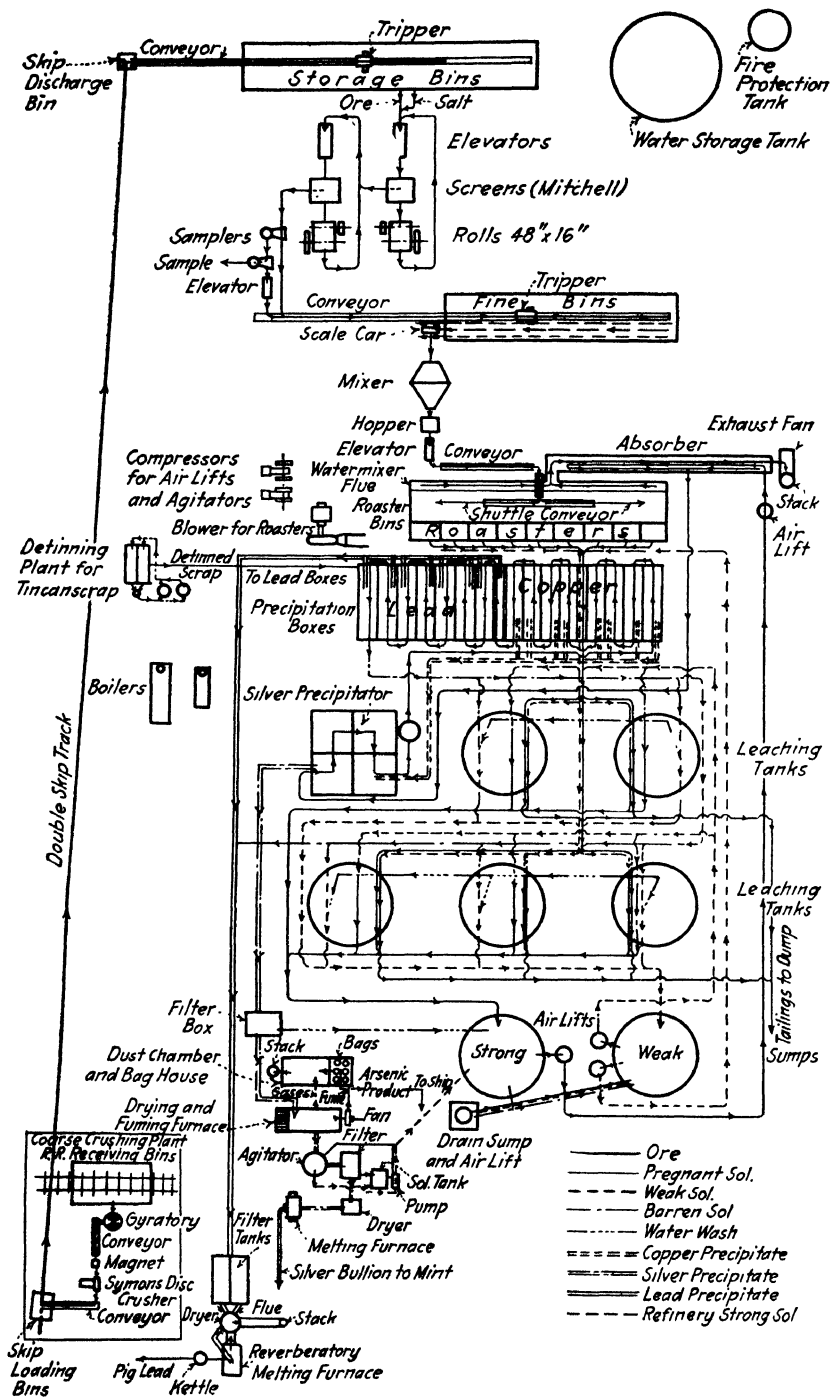


FIG. 3.—GENERAL FLOW PLAN OF PLANT.

STRUCTURAL AND MECHANICAL FEATURES

The process described was adopted after numerous tests made on the ore with various processes, such as concentration, flotation, volatilization, and cyanide, as it gave a higher and more consistent recovery at a reasonable cost than any of these. Owing to its nature, however, materials that could be used in the construction of the plant were practically limited to wood, siliceous concrete, and rubber. The structural and mechanical features may be of some interest. The general flow plan, Fig. 3, approximately indicates the arrangement and flow of ore and solu-

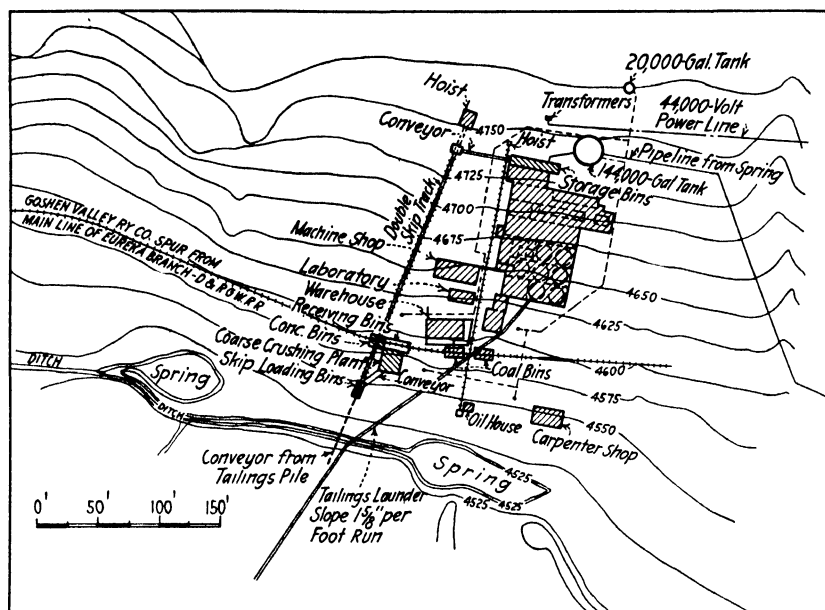


FIG. 4.—GENERAL ARRANGEMENT OF PLANT.

tions through the mill. The general ground arrangement of the plant, which is situated on a hillside, having a slope of 29° is shown in Fig. 4.

The railroad, entering the plant below the main mill building, delivers ore, salt and coal to bins, and the preliminary crushing plant, from which they are hoisted, in 45-cu. ft. skips, up a double-track incline, to a conveyor distributing to the storage bins at the top of the mill. A service tramway, with skip operated by a 50-hp. hoist, runs from the bottom of the hill alongside the mill building to the top ground floor, serving all floor levels, together with the machine shop, laboratory, warehouse, crushing plant, and carpenter shop, which are situated along this tram. The warehouse is also on the railroad; and all materials received can be delivered to any department of the plant with this skip.

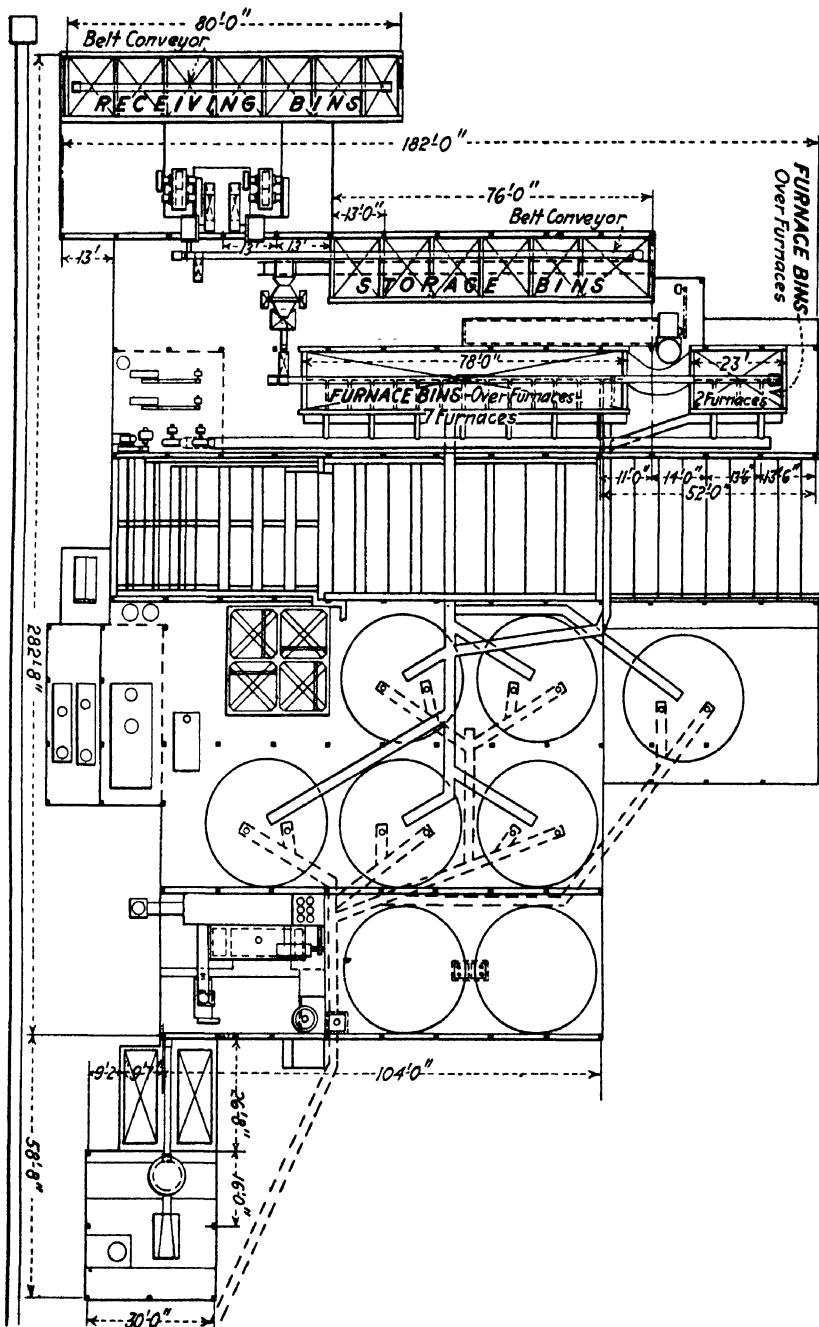


FIG. 5.—GENERAL PLAN OF MILLING PLANT.

BUILDINGS

The buildings are of wood, the sides being covered with a double thickness of 1-in. boards, with 40-lb. building paper between, and the roofs with extra heavy Rubberoid laid on 1-in. boards.

The main mill building is approximately 282 ft. long and 182 ft. wide, with an extreme height of 40 ft. and an average height of 24 ft. There are no special features in the design, but all floors or sections spanned by trusses are of the same width, 33 ft., so that all trusses are exactly alike, which results in economy in construction. The slope of the roofs was

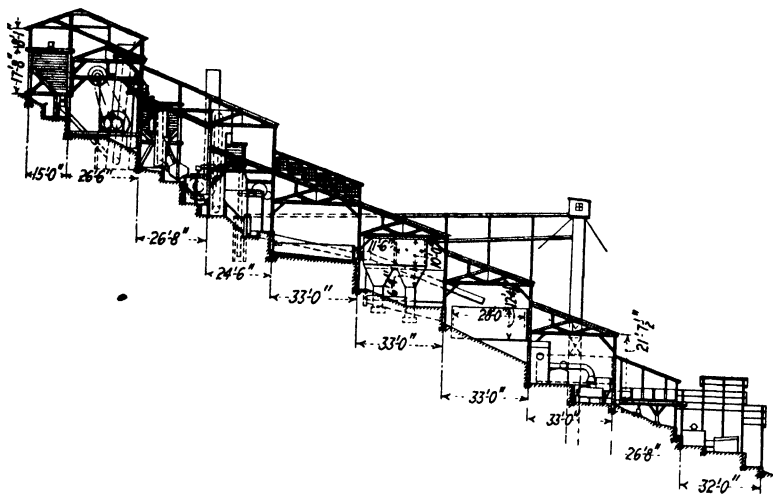


FIG. 6.—GENERAL CROSS SECTION OF MILLING PLANT.

so made that, with this span, a minimum of material consistent with required strength was realized. All bents are 13 ft. wide. All foundations and retaining walls are of reinforced siliceous concrete, and all the ground in the wet part of the mill is covered with a concrete coating, terminating in a general drainage sump in the lower end of the mill. Figs. 5 and 6 show the general plan and general cross-section, or sectional elevation of the mill.

CRUSHING

The tests indicated that the finer the crushing, the better was the recovery; but at the same time a granular product was necessary for the roasting and leaching operations. So in the design, attention was first directed to this step in the process and a crushing scheme was adopted and equipment selected that would fulfil this condition to the fullest extent possible. These are indicated on the general flow plan; the screen analysis previously given shows the product realized.

A gyratory followed by a Symons disk for the preliminary or coarse crushing, and large rolls and screens, in series, the screens preceding the rolls, so that fines are eliminated as fast as produced without further grinding, were adopted as being the most suitable for producing the desired result. The centrifugal action of the Symons in immediately discharging everything below the size to which the disks are set produces a minimum of fines; and as the ore is dry, the machine gives no particular trouble. One set of manganese-steel disks crushes between 40,000 and 50,000 tons. An electromagnet is suspended over the short conveyor belt between the gyratory and Symons disk to remove tramp iron. Expressed in terms of original ore, the life of the coarse roll shells is about 25,000 tons; and of the fine roll shells about 30,000 tons. Each shell weighs 3000 lb.

The gyratory and Symons disk are driven from a line shaft by a 50-hp. motor, and run about 5 hr. out of the 24. A 125-hp. motor drives the rolls and elevators through a line shaft; they run about 20 hr. daily.

The fine ore and coal are withdrawn from the fine storage bins into a hoppers scale car, carrying 3000 lb., which is propelled by trolley and discharges into an ordinary tilting concrete mixer, which, in turn, delivers through hopper and belt feeder to an elevator. A belt conveyor receives the discharge of the elevator, and delivers it to a paddle mixer, where it is moistened. A shuttle conveyor directly beneath the paddle mixer distributes the product to the roaster bins.

HOLT-DERN ROASTERS

The inception and early development of the roaster is described by Theo. P. Holt;¹ as used in this plant, it is shown in Fig. 7. There are nine of these—seven in one bank and two in another. The general structure is of reenforced, siliceous concrete. The roasting chamber sides are $\frac{1}{4}$ -in. steel plate, lined with 6 in. of concrete; the ends, which are formed by the 10-in. partition walls, have also an additional 6-in. concrete lining. This lining gradually disintegrates and must be renewed about once a year.

At the bottom of the roasting chamber, there are fifteen rocking grates, 7 ft. long, spaced $7\frac{3}{4}$ in. apart. Each consists of a $2\frac{1}{4}$ -in. square steel shaft, passing through the cast-iron grate bars, which are made in sections 21 in. long, and are shown in cross-section. They have four longitudinal ribs, $1\frac{1}{2}$ to 2 in. high, 90° apart, the vertical ribs being solid, while the horizontal ribs are notched for free passage of the air through the grates. When the top rib is worn down, the shaft is turned over and the opposite rib used; when both are worn they are replaced with new bars. These bars wear about $1\frac{1}{2}$ years. The grates rock through an angle of 60°, and are actuated in pairs by segmental gears

¹Trans. (1914) 49, 188.

on each shaft, which are given a reciprocating motion through connecting rods by two main cranks. These are revolved through bevel gears and pinions from a line shaft, each pinion being attached to a friction clutch, which is keyed to the shaft. Thus half of the grates in a roaster can be operated at a time, and the starting load is only one-half as large. The grate shafts pass through stuffingboxes, with glands in cast-iron plates, in each side of the roaster. On the gear, or driving, side, they turn in rigid bearings that are supported on a cast-iron filling piece resting on a 12-in. I-beam; on the opposite side, the glands of the stuffingboxes serve as bearings. The bearings are specially designed, with caps fitting

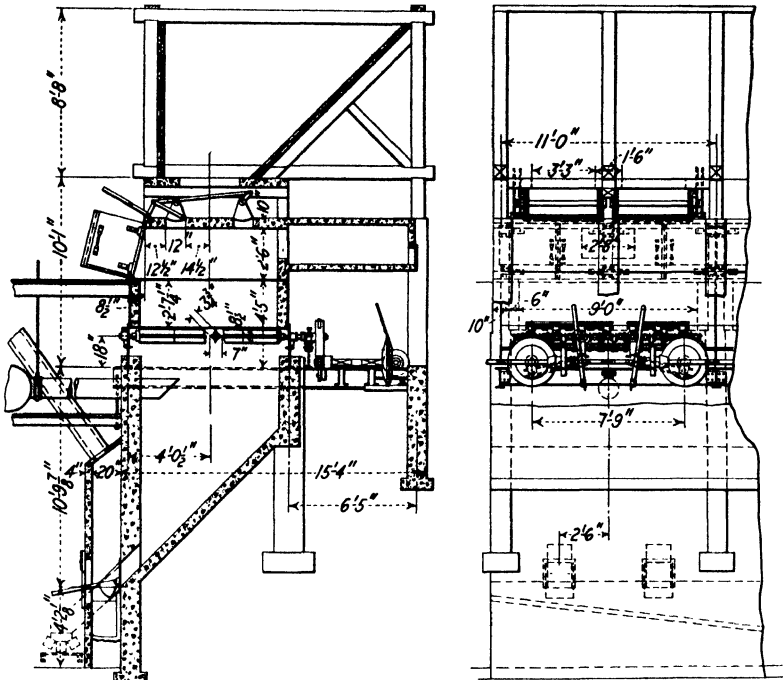


FIG. 7.—HOLT-DERN ROASTER.

accurately in deeply machined grooves and a dowel between the bases and the cast-iron support, so that the shafts are held firmly in place. The gears are thus held in mesh always on their pitch lines and there is no sliding contact, so that the wear of the teeth is reduced to a minimum and any lost motion is prevented in the movement of the grates—an important feature. The whole mechanism is so designed that any bearing, or any other part, can be quickly and easily repaired or replaced, so that there may be no delays in the operation of the roaster and the roast can always be quickly discharged. The line shaft is driven by a 15-hp. motor on each end, one of which is a spare; from 2 to 5 hp. is required

for each motor after starting. If the charge is "hard," or partly sintered, double this power is sometimes required to start the grates. From 5 to 15 min. are required to "drop" or discharge the roasted charge.

The Sturtevant gas blower, supplying air to the nine roasters at 8 oz. pressure, has a capacity of 15,000 cu. ft. per min., and is direct connected to a 75-hp., 1800-r.p.m. motor. There are two of these, one being kept in reserve.

The gases issuing from the roasters have a temperature of only 35° to 55° C., so that an exhaust fan is necessary to remove and discharge them through an absorbing chamber and short stack. This fan is



FIG. 8.—ROASTER MECHANISM BEFORE GRATE SHAFT BEARINGS WERE ADDED.

72 in. in diameter, 35 in. wide, and is housed in a concrete casing. It is driven by a 15-hp. motor at 250 r.p.m. Originally, the fan runner was completely rubber covered; now only the spider is rubber covered and the blades, which are of $\frac{3}{16}$ -in. steel, are painted with six coats of elaterite paint. This coating lasts three to four months. The stack is 5 ft. in diameter and 40 ft. high and rests on top of the fan casing. It is made of 3 by 6-in. plank with round iron bands, similar to wood-stave pipe.

LEACHING TANKS, PRECIPITATING BOXES, AND TANKS

These are all of reenforced, siliceous, concrete, and great care was exercised in the designs, preparation of the materials, and placing of the concrete. The aggregate was composed of crushed quartzite, taken from one of the mine dumps, and siliceous sand, part of which consisted of fines from crushing the quartzite, the SiO_2 content being 96 per cent. The walls and bottom of tanks are 8 in. thick, while those of the precipitation boxes are from 5 to $7\frac{1}{2}$ in. Test blocks were made in all cases, and a

mixture made up to stand 2500 to 3000 lb. per sq. in. in compression, while the reenforcing steel was calculated on a basis of 10,000 lb. per sq. in. safe tensile strength. The true mix varied from 1:3 to 1:4, and the maximum size of the aggregate was $1\frac{1}{4}$ to $1\frac{1}{2}$ in. The proportions of coarse and fine aggregate were about 65 and 35 per cent., respectively, and none of the concrete has shown any penetration or leakage of solution. There are two circular discharge holes 13 in. in diam. in the bottom

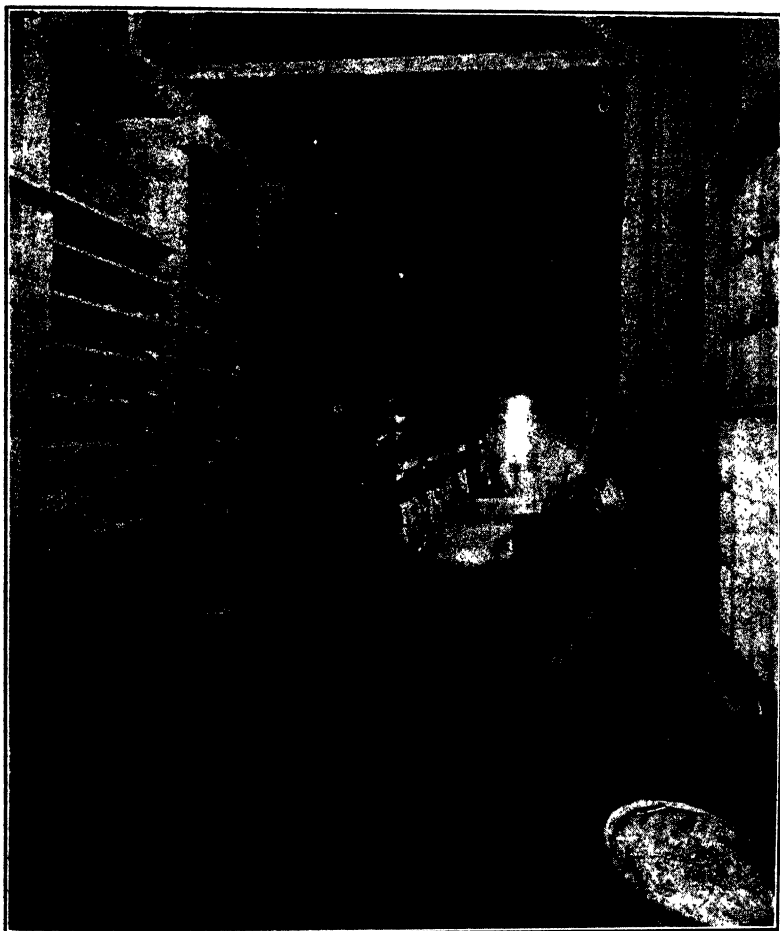


FIG. 9.—ROASTER WORKING FLOOR.

of each tank; and on the underside a circular dovetail groove, $\frac{5}{8}$ in. deep, $1\frac{1}{4}$ in. wide on the bottom, and 1 in. on top was cast around each hole. A soft-rubber packing ring to fit this groove, and thick enough to project $\frac{5}{8}$ in. from the concrete is inserted. The gate, made of two thicknesses of 3-in. plank, doweled together with wooden pins, is drawn up against the rubber packing ring by means of a rubber-covered $1\frac{1}{4}$ -in. rod extending

through the tank and a beam 2 ft. above the top, which is supported by two posts resting on the tank bottom. The two 3-in. stoneware cocks for discharging solution are screwed into wooden nipples set in the sides of the tank just at the bottom. The quartzite gravel, forming the filter bottom, rests on triangular strips that are supported by 2 by 4-in. pieces lying on the tank bottom. These strips were made by ripping 6 by 6-in. sticks diagonally, and are held apart by small pieces.

The silver precipitators were made of about the same mix as the leaching tanks, with the same proportion of steel; but a 1:5 mix was used in the construction of the copper and lead precipitation boxes. There is no deterioration or penetration of the concrete, even by the hot solutions in the lead precipitation boxes; but as these are decanted and washed out at frequent intervals with cold water, cracks occasionally develop, which are simply chipped out and filled in with a 1:1 cement mortar. On the other hand, the walls of the absorber chamber, where the roaster gases are drawn horizontally through falling sprays of solution, do not endure. The cement is gradually dissolved and the walls disintegrate. They are now protected with elaterite painted plank, which lasts over a year. The sides of the fan casing have also softened to a depth of $\frac{3}{4}$ in., but they remain this way without disintegrating and it has been unnecessary to repair them.

AIR LIFTS

Solutions are pumped from the sump tanks at the lower end of the plant to the sluice launders under the roaster hopper discharge gates, the absorber, precipitators, and the leaching tanks with four air lifts, made of bored redwood pipe, two of which are 5 in. and two 4 in. inside diameter. These lifts are supported by the tower shown near the lower end of the mill in Fig. 6. The net lift is 60 ft. above the top of the tanks, and submergence is obtained by a two-compartment concrete-lined shaft 60 ft. deep, connected with the sumps. A 1-in. rubber-covered air hose enters each of the pumps a few feet above the top of the tanks, and extends down to about 18 in. from the bottom. The pipe lengths are from 8 to 14 ft. and the joints of the submerged portion are held together with four 2 by 10-in. planks 5 ft. long, doweled to the pipe with wooden pins. Iron clamps, 2 to 3 ft. apart, are put on the unsubmerged part to prevent splitting. Each pump terminates, on top, in a discharge barrel 32 in. in diameter and 42 in. deep, which discharges into a launder. Air is supplied at 40 lb. pressure for the air lifts and silver precipitators by three motor-driven compressors, having a total capacity of 900 cu. ft., which is more than ample, so that when repairs are necessary on any one, pumping is not interfered with. The 5-in. pumps will each handle 130 gal. per min., and the 4-in., 110 gal. These air lifts are quite satisfactory, except that occasionally a crack develops in the submerged portion, requiring the

pulling of the pump and replacing of the broken length; which is slow, arduous, and somewhat expensive. Two 2-in. centrifugal "Olivite" pumps handle barren solution with lifts of about 20 ft. In these, the casing is lined and the runner covered with a composition that is not affected by the solutions. They discharge through rubber-lined pipe, which so far has shown no deterioration. These pumps may, in time, replace the air lifts.

The solutions are carried about the plant in wooden launders made of 2-in. plank, held together with clamps, but the wood shrinks and softens, especially from the hot solutions, making it very difficult to prevent leaks. To overcome this, the solution launders are lined with a cement mortar, made of one part siliceous sand, one part quartzite gravel of a maximum size of $\frac{3}{8}$ in., and a two-thirds part of cement. Wire netting, 1-in. mesh, is placed in the launder, conforming to the sides and bottom, together with some $\frac{1}{4}$ -in. rods, the launder partly filled with the mortar, and the inside forms, made in 6- or 8-ft. lengths, are then set in and pressed into the mortar, forcing it up on the sides, when it is rammed and levelled up to the top. The bottoms of the sluicing launders carrying the hot roasted ore in solution are lined with concrete slabs of the above mixture, 30 by 16 by $1\frac{1}{2}$ in., cast in separate molds and cured for several days. Slabs 7 in. wide are used on the sides. A concrete air agitation tank, 8 ft. deep and 4 ft. in diameter, in which the oxidized copper is leached out of the silver precipitates with a hot 25 per cent. sulfuric-acid solution, slowly disintegrated, but a sulfur-and-sand lining, made of equal parts of melted sulfur and fine sand, thoroughly mixed and poured in a form, making it $1\frac{1}{2}$ in. thick, has stood very well. Care must be used to keep the temperature of the sulfur just above the melting point, and to pour the mixture quickly before the sand settles out.

HEATING OF SOLUTIONS

Steam for heating the solutions is supplied by three boilers, two of which, aggregating 110 hp., supply steam to the copper coils, the condensation returning to the boilers through a trap. The coils become coated with a hard scale, precipitated out of the solution, which gradually lowers their efficiency until it becomes necessary to knock off the scale. The other boiler, a 125-hp. return tubular, supplies live steam direct to the solutions in the precipitation boxes, after it has passed through the coil box, and to any other places where steam is required. While this is the normal method of running, a double system of steam piping permits the steam from any one, two, or the three boilers to be run to either the coil or live steam systems. The three boilers consume about 11 tons of slack coal per day, and 1000 tons of solution are heated from 48° to 75° C.

GENERAL

Water supply for the plant is pumped from a spring at the base of the hill to a 140,000-gal. wooden storage tank above the mill, by a 250-gal. per min., triplex pump, driven by a 30-hp. motor, running 18 hr. daily; the net lift is 225 ft.

Power is delivered to the plant at 44,000 volts, by the power company, transformed to 2200 volts for all motors over 30 hp., and to 220 volts for all under that size. The motors are all wired with three-conductor lead-covered cable, and all wiring for lights is lead encased. The total connected load amounts to 700 hp., but the average maximum demand reading is about 500 hp.

Well-equipped machine and carpenter shops enable practically all repairs to be quickly made at the plant. As the process as a whole is rather destructive, the repairs are considerable, but the plant has now been in operation $4\frac{1}{2}$ years without a shutdown.

DISCUSSION

T. VARLEY, Salt Lake City, Utah.—On page 324, the authors say that for consistent results a small amount of free acid is necessary in the solution; also that small amounts of copper sulfate are added to the brine. On the next page, they say that trouble has been experienced when working with a solution saturated with respect to salt. Possibly one reason is the effect the solution might have on the calcines; in the upper strata of the calcines extraction of silver is good while in the lower strata extraction is relatively poor. It may be well to determine if at that point there is crystallization of the salt or a large consumption of acid, either of which would tend to upset the balance.

Calcium chloride is used only in extreme cases for chlorine concentration; in view of the cost it might pay to study the possibilities of making calcium chloride at the plant, utilizing some of the byproducts for the flotation plants in the district. Chlorine, potassium, and magnesium are present in large quantities in the desert brines west of Salt Lake City, and a careful investigation may develop a source of calcium chloride as well as other byproducts.

H. R. HANLEY, Rolla, Mo.—Is the precipitation in the tin-scrap tank complete? Also, what are the relative merits of tin scrap and sponge iron, taking into consideration the difference in temperature required by the solutions in the various processes?

H. P. ALLEN, Payson, Utah.—The precipitation of the lead on the tinplate is very nearly complete. For instance, the heads are 0.7 and 0.8 per cent. and the tails solutions are 0.03 and 0.02 per cent. lead. That is dependent on the temperature and the surface exposed in the precipita-

ting boxes. With sponge iron, the rate of precipitation is much more rapid and it does not require as high a temperature as does precipitation on tinplate cuttings. But the problem is to get the sponge iron in sufficient quantities and cheap enough to make its use commercially feasible. The Bureau of Mines has done extensive and good work on the precipitation of lead on sponge iron. It has perfected a small portable apparatus, which was placed in our plant and run very successfully for a number of days.

G. H. DERN, Salt Lake City, Utah.—The question is often asked, "Why is there such an economy of fuel in the Holt-Dern roaster?" Fuel economy implies conservation of heat. In all ordinary furnaces the loss of heat, and consequent high fuel consumption, is due to three causes: (a) The waste gases being discharged to the stack at a high temperature; (b) the finished product being discharged from the furnace at a high temperature; (c) radiation from the furnace itself.

The Holt-Dern roaster in a large measure overcomes these losses. It is a blast roaster, the roasting being done by combustion of the fuel contained in the ore charge. The fuel is mixed with the ore and no extraneous heat is applied.

The roasting charge is a descending vertical column. The upper portion is a layer of raw, moist ore; the middle portion is the roasting zone; the bottom portion is a layer of roasted ore or calcine. The air blast, which induces combustion, travels upwards through this column. First striking the hot calcine, the blast is preheated and the calcine is correspondingly reduced in temperature. Not all the waste heat is used, but loss (b) is materially reduced.

As combustion takes place in the mass of the charge, there is no loss of heat by radiation as is the case when a flame plays over the surface of a bed of ore. A lighter-than-air flame always keeps as far above the bed of ore as the construction of the furnace will permit and is constantly seeking a way to the stack without touching the ore. In blast roasting, the heat cannot go toward the stack except through the ore mass, hence the most intimate contact and the minimum of loss (c).

The waste gases from the roasting zone must pass through the layer of moist, raw ore at the top of the column. The descending ore is thereby preheated and the waste gases are discharged from the stack at a temperature so low that the hand may be held in the furnace above the roasting column, thus largely eliminating loss (a).

The travel of ore is counter-current to the air blast, which results in conservation of heat and economy of fuel. About 3 per cent. of coal is all that is needed to roast oxidized ore as in chloridizing. Ore carrying the proper proportion of sulfide is self-roasting and requires the admixture of no other fuel.

Another question that is invariably asked is: "Why is there no loss by volatilization in the Holt-Dern roaster?" My explanation has always been that any metals that are volatilized in the roasting zone are condensed when they strike the layer of moist cool ore at the top of the charge. Recently Mr. Holt suggested that in the lower part of the roasting zone the gases are strongly oxidizing, becoming lower in oxygen as they pass up through the charge; this gives an ideal finishing condition for the roast, insuring the complete elimination of undesirable compounds. When the air reaches the upper part of the roasting zone, where compounds that oxidize with great rapidity are present, it is so depleted of oxygen that the danger of excessive heating is largely eliminated. In other words, the result is a uniform temperature throughout the roasting charge. As the gases enter the zone of raw ore at the top of the charge they are reducing in character, being highly charged with sulfur dioxide. Any volatile metal compounds that would otherwise pass to the stack are reduced and remain in the ore.

When roasting is in progress, the charge is quiescent. There is no rabbling and the only dropping is when the calcine is shaken into the closed bin beneath the grates. The top of the roasting column is moist ore. These conditions practically preclude dust loss.

The authors give a full description of the mill and cite operating costs. It will be noted that the ore is delivered at the bottom of the mill instead of at the top and that the coarse-crushing department is the lowest part of the plant. From here the ore is hoisted to the top of the mill for successive fine crushing, mixing, roasting, and leaching. This type of construction was adopted to save large additional railroad construction, but it increases the cost of operation. Salt, coal, and all other supplies are subject to extra handling cost on account of this arrangement. The plant is not ideally designed for cheap operation.

The total cost of crushing to 8 mesh is \$0.714 per ton, including unloading the railroad cars. To one familiar with roll crushing this looks high. At the Consolidated Mercur Gold Mines Co., of which I was general manager, we crushed to 5 mesh for 8 to 10 cents per ton, before the war, but that ore was exceptionally soft and easy to crush. I understand that the Utah Copper Co. crushes dry to -8 mesh for $8\frac{3}{4}$ cents per ton, and to -60 mesh for a total of 22 cents, the fine grinding being done wet. The Tintic Milling Co., using the same process as the Tintic Standard, crushed Tintic ore for about 60 cents per ton under unfavorable conditions with small old-style rolls, inadequate screens, and the excessive elevating and conveying made necessary by a flat mill site. With proper equipment, the cost in that plant could have been materially reduced. The relatively high crushing cost at the Tintic Standard is due to the location of the coarse-crushing department, the extraordinarily hard and tough charac-

ter of the ore, and the relatively small scale of operations — 200 tons per day.

A plant properly designed for gravity operation on a scale of 1000 tons per day could crush to the size stated for about 35 cents. The crushing costs reported in the paper, therefore, are not a criterion of the necessary costs for this process.

The roasting cost of \$1.148 includes the salt and the expense of remodeling the roaster drive. Repairs and renewals have been greatly reduced since this alteration was made. Not long ago I estimated that the roasting cost in a proposed 1000-ton mill would be 25 cents per ton, exclusive of salt.

Leaching, precipitating, and treatment of precipitate are much higher in this plant, where copper and lead are recovered, than they would be in a straight silver mill, or even on a silver-copper proposition. The lead recovery entails heating the leaching solution as well as separate precipitation. Chloride roasting and leaching have decided advantages where the conditions are favorable for their use.

Milling Practice at Midvale

By C. A. LEMKE,* MIDVALE, UTAH

(Salt Lake City Meeting, September, 1925)

THE ores now milled at the Midvale concentrator of the United States Smelting, Refining & Mining Co. come mostly from the company's mine in the Bingham district, about 18 miles west of Midvale. Custom ores from this same district and from other western mining districts are also milled at times.

The Bingham ores consist of galena, pyrite, chalcopyrite, and sphalerite in a gangue of quartz, quartzite, limestone, and porphyry. The percentage of chalcopyrite is small, usually about 0.5 per cent., while the galena, pyrite, and sphalerite combined constitute about 60 per cent. of the total ore. These three minerals vary considerably in amount and, at times, all three are somewhat oxidized. The ores also contain gold and silver, the former being mostly in the pyrite while the latter is generally with the galena. The crystallization of the economic minerals varies from fairly coarse to extremely fine.

The ores are carried to Midvale by the Bingham & Garfield and the Los Angeles & Salt Lake railroads or by the Denver & Rio Grande Western railroad, in 50-ton, steel, full dump cars.

The milling problem is to recover the silver-bearing galena, the gold-bearing pyrite, and the chalcopyrite in a product suitable for the lead smelter and containing the least possible amount of gangue and sphalerite and then recover the sphalerite in a product suitable for a zinc smelter. The minerals are recovered partly by water concentration and partly by water concentration combined with electrostatic treatment.

GRAVITY CONCENTRATOR

The gravity concentrator has a capacity of about 465 tons in 24 hr. The mill buildings are of wood. The mill was built in 1905 to handle approximately 90 tons in 24 hr.; since that time several additions have been built and various changes have been made in the flow sheet. The last extension, which raised the capacity of the mill to its present level, was built in 1915. The additions to the mill building have not kept pace with

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the increase in the tonnage milled. The present floor space is about twice that of 1905 while the tonnage handled is over five times as great. This has made it necessary to place concentrating and crushing machinery where the space was inadequate and has resulted in considerable crowding.

The ore is dumped from the railroad cars into a hopper-shaped bin of 250 tons capacity. From this bin, it is fed, by hand through a rack-and-pinion gate and over a stationary grizzly to a 10 by 20-in. Blake crusher. The grizzly has $1\frac{1}{2}$ -in. openings and the crusher is set to crush to this same size; approximately 25 per cent. of the average run of ore passes through the grizzly. The crusher discharge, combined with that from the grizzly, passes to a bucket elevator, which discharges into a 72 by 42-in. trommel. The screen on this trommel is $\frac{1}{4}$ -in. punched plate with $1\frac{3}{16}$ -in. round holes. The trommel undersize passes to the crushed-ore bin; it is sampled by an automatic sampler before going into the bin. The trommel oversize goes to a set of 30 by 12-in. rolls, which are in closed circuit with the trommel. From the crushed-ore bin, which has a capacity of 150 tons, the ore is fed by means of a plunger feeder to No. 2 elevator, which discharges into two 72 by 36-in. trommels. Water is added in the boot of the elevator. The trommels have punched-plate screens with $\frac{5}{16}$ -in. round holes. The oversize from the trommels goes to a set of 36 by 16-in. rolls and, after passing through the rolls, is returned to the trommels by way of No. 2 elevator. All of the mill feed must pass through the $\frac{5}{16}$ -in. screens before concentration begins. The undersize from the $\frac{5}{16}$ -in. screens goes to the jig-screen line, where the jig feed is divided into four sizes. This screen line consists of a double row of trommels, each trommel being 5 ft. long and 3 ft. in diameter. The first two trommels have 4-mesh screens; the undersize from the $\frac{5}{16}$ -in. punched-plate screens passes to these two trommels, the feed being equally divided between the two. The second two trommels in the row have 6-mesh screens; and the third two 8-mesh screens. All screens on these trommels are steel-wire cloth with square openings. The openings in the 4-mesh screens are 0.13 in., in the 6-mesh 0.087 in., and in the 8-mesh 0.053 in.

The 4-mesh screens discharge their oversize to No. 1 jig and the undersize to the 6-mesh screens; the oversize from the 6-mesh screens goes to No. 2 jig and the undersize to the 8-mesh screens, the 8-mesh oversize goes to No. 3 jig and the undersize to a 42-in., double-cone, hydraulic classifier. The spigot produce from this classifier goes to No. 4 jig and the overflow product to the table circuit, which will be discussed later.

JIGS

All jigs are Hartz type, single, three-compartment, except No. 4 which is a double three-compartment jig. All jig compartments are 36 by 24 in. The openings in the jig sieves are larger in every case than the

largest particle fed to the jig and all jig concentrates are hutch products, there being no side discharge gates on any jig. The high percentage of metals in the ore requires that the concentrates be discharged rapidly. When operating the jigs, the aim is to make a lead-iron concentrate with the highest possible recovery of lead and iron and containing the lowest possible percentage of zinc and gangue. About 60 per cent. of the total lead recovered in the mill is taken out by these four jigs. The zinc and gangue present in the jig concentrates are mostly in the form of combined particles. The lead-iron concentrates from the four jigs average about 25 per cent. lead, 24 per cent. iron, 10 per cent. zinc, $3\frac{1}{2}$ per cent. gangue, 12 oz. silver, and 0.15 oz. gold. The concentrates from Nos. 1, 2, and 3 jigs are discharged from the hutches intermittently, by hand, through ordinary molasses gates; and those from No. 4 jig are discharged continuously through a spigot. The stroke and speed of the jig plungers are as follows:

Jig	STROKE LENGTH, INCHES	NUMBER PER MINUTE
No. 1.....	$1\frac{1}{4}$	185
No. 2.....	$\frac{3}{4}$	215
No. 3.....	$\frac{1}{2}$	245
No. 4.....	$\frac{1}{4}$	285

The bedding for all jigs is replenished by hand as it wears out.

The tailings from the jigs are dewatered in a 30-in. dewatering or shovel wheel and go to a set of 36 by 16-in. rolls. The shovel-wheel overflow is sent to a 9-ft. cone tank and the overflow from this tank goes into the mill tailings, as it is practically clear water. The cone-tank spigot product is sent to the table circuit. After passing through the rolls, which are set to crush to 12-mesh, the jig tailings go to No. 3 elevator, which discharges into two 5 by 3-ft. trommels fitted with 12-mesh steel-wire screens. The undersize from these screens is sent to the classifier system. The oversize goes to another set of 36 by 16-in. rolls and back to No. 3 elevator.

CLASSIFIERS

All classifiers in the mill are of the double-cone free-settling type. Other classifiers have been tried at various times but none showed sufficient improvement over the work done by the double-cone type to warrant their permanent installation. The double-cone classifiers vary in size from 20 to 42 in. (the dimension being the diameter of the inner cone). The classifiers are set in such a way that the overflow from each goes to the inner cone of the next succeeding one. The one with the smallest inner cone receives the undersize product from the 12-mesh screens. The overflow from the last classifier goes to a series of cone tanks. The spigot products from the first two classifiers, which are both 20-in. classifiers, are sent to a three-compartment, 24 by 36-in.,

Hartz jig, called No. 5 jig. The spigot of the third classifier goes to another jig of the same size, called No. 6 jig.

Nos. 5 and 6 jigs make lead-iron concentrates and tailings. The tailings are reground in tube-mills, classified and tabled. These jigs are operated in the same manner as the first four jigs.

TABLES

The spigot products from the fourth and succeeding classifiers are sent to thirteen tables, six of which are Deister Plato, five are No. 6 Wilfley, and two are the old type Overstrom. The two Overstrom tables are used on the finest sizes. The first four tables, which handle the coarser sizes, make lead-iron concentrates, middlings, and tailings to waste. The middlings are sent to the tube-mills along with the tailings from No. 5 and 6 jigs. The last nine tables also make lead-iron concentrates, middlings, and tailings, but the middlings are not reground because they usually contain only a small percentage of combined mineral. They are, in reality, a mixed product rather than a middling. This material is retreated on six Wilfley tables, which make a small amount of lead-iron concentrates, zinc-iron concentrates, middlings and tailings; these tables are called retreatment tables. The zinc-iron concentrates are sent to the electrostatic mill and the middlings are returned to the classifiers, which feed tables Nos. 5 to 13. This so-called middlings product is cut out on the retreatment tables between the zinc-iron concentrates streak and the tailings streak because the zinc-iron concentrates must contain less than 6 per cent. insoluble and if a direct cut was made between concentrates and tailings there would be considerable danger of exceeding this limit.

The back water on tables Nos. 4 to 13 contains considerable slime; this back water is sent to a 4-in. Wilfley sand pump, which discharges into an 8-ft. cone tank. The spigot from the cone tank is sent to a Wilfley table and the overflow goes, by way of a distributing launder, to fourteen 8-ft. Callow tanks. These Callow tanks feed the seven slime tables, two tanks feeding one table. The cone tank that receives the Wilfley pump discharge takes out any coarse sand that might be taken up with the table back water. The overflow from the last tank in the classifier line is sent to the same distributing launder that handles the overflow from the Wilfley pump tank.

SLIME TABLES

The Deister slime tables, which are fed from the fourteen 8-ft. Callow tanks, make lead-iron concentrates, zinc-iron concentrates, a mixed product, and tailings to waste. The zinc-iron concentrates are sent to the electrostatic mill and the mixed product from all seven tables is

retreated on one Deister slime table, which makes zinc-iron concentrates and tailings to waste.

TUBE-MILLS

The tailings from Nos. 5 and 6 jigs and the middlings from the coarse-sand tables are combined and sent to a 30-in. dewatering wheel. The sand discharge from this dewatering wheel goes to a bin of 50 tons capacity, and the overflow from the wheel box, which contains some slime and fine sand, is sent to an 8-ft. cone tank. The cone tank overflow goes into the mill tailings and the spigot product is treated on a Wilfley table, which makes the usual products. The dewatered sand is fed from the 50-ton bin to the tube-mills, of which there are two. These mills are 14 ft. long and 5 ft. in diameter. Usually only one tube-mill is used, but occasionally the ore contains considerable quartzite, which is very hard and it becomes necessary to use both. The tonnage ground in the tube-mills averages about 130 tons in 24 hr., or approximately 28 per cent. of the original mill heads. In operating the tube-mills, the aim is to grind just fine enough to liberate the minerals and produce the least possible amount of slime. On the average run of ore, practically all of the galena and sphalerite are liberated when the ore is crushed to 48-mesh, although at times finer grinding is necessary. When the tube-mill product is all -48-mesh, approximately 22 per cent. will pass a 200-mesh screen. An average screen analysis of the tube-mill feed and product is as follows:

TUBE-MILL FEED			TUBE-MILL PRODUCT		
MESH	SCREEN SIZE OPENING, INCH	PER CENT. ON	MESH	SCREEN SIZE OPENING, INCH	PER CENT. ON
14	0.046	4.9	14	0.046	0.0
20	0.0328	20.7	20	0.0328	0.0
28	0.0232	29.1	28	0.0232	1.1
35	0.0164	20.2	35	0.0164	2.8
48	0.0116	13.5	48	0.0116	6.1
65	0.0082	9.3	65	0.0082	18.4
100	0.0058	2.3	100	0.0058	23.8
			150	0.0041	13.4
			200	0.0029	12.1
			-200	0.0029	22.3

The tube-mill product is sent to No. 5 elevator, which discharges into the first of a series of eight double-cone hydraulic classifiers. The classifiers feed eight Wilfley tables, which make lead-iron concentrates, zinc-iron concentrates, zinc-iron-gangue middlings and tailings. The zinc-iron concentrates go to the electrostatic mill and the middlings to four Wilfley tables, which make zinc-iron concentrates, middlings, and tailings. The middlings from these four tables are returned to the tube-mills. The overflow from the last of the eight hydraulic classifiers

goes to an 8-ft. cone tank. The tank spigot product is treated on a Wilfley table and the overflow goes to the Callow tanks, which feed the Deister slime tables. The back water from the Wilfley tables is pumped to these same tanks.

The tube-mills are lined with ribbed cast-iron liners. The ribs are about $\frac{1}{2}$ in. thick and $3\frac{1}{4}$ in. high; the backs of the liners are about $\frac{3}{4}$ in. thick. The liners are 6 in. wide and of such length that four make a complete circle. Two liners in each circle, or ring, have one end flanged in such a way that the flanges overlap when the two liners are placed end to end with the flanges adjacent. By tightening the nuts on a short rod, which is passed through opposite holes in the flanges, the four liners in each ring are wedged tightly against each other and against the shell of the mill. There are twenty-five complete rings in the mill and three rings from which a section have been cut to make room for the manhole frame. This frame is of the same height as the ribs on the liners and is held in place by the liners. The only through-bolts used on the shell liners are two in the manhole-cover lining. The life of the lining has been increased from 11 to 14 months by cementing fragments of quartzite around the short rods that hold the liners in place. Cement grout is poured into any small opening that may occur between the rows of liners, because of rough or uneven castings, to protect the shell. The end liners are bolted to the heads of the mill with countersunk through-bolts. The grinding medium used at present is "adamant silica" in the form of cubes with edges $3\frac{1}{2}$ to $4\frac{1}{2}$ in. long. This material has proved to be as satisfactory as the foreign flint pebbles formerly used and it is cheaper. The grinding medium, by wedging in between the ribs of the cast-iron shell lining, also forms the principal wearing surface of the mill. The consumption of "adamant silica" is about 1.25 lb. per ton of ore ground. The pebble load carried in the mill averages about 10,200 lb. The mills require about 35 hp. each.

HANDLING OF CONCENTRATES

All lead-iron concentrates from the jigs are carried, by means of launders, from the jig hutches to a bucket elevator. About 85 per cent. of the sand-table concentrates are also sent to this elevator. The remaining 15 per cent. of sand-table concentrates cannot be carried by gravity to this elevator; these are shoveled out of the catch-boxes into mine cars and trammed to railroad cars. The concentrates elevator discharges into a launder, which carries the product to five hopper-shaped bins of 50 tons capacity, each. The sloping bottoms of these bins are made of 4-mesh, galvanized, steel-wire screen laid on 2 by 4 in. joists spaced 9 in. apart. The screen is covered with a layer of burlap and on top of the burlap is a layer of cocoa matting. Under the sloping bottoms is a water-

tight floor, which has a slope of $\frac{1}{2}$ in. per ft. toward one edge. A launder at the lower edge of the floor carries the water from the concentrates to either of two small settling ponds. These ponds are cleaned out every month. The tops of the bins, also, have overflow launders, which carry away some water when the bins are nearly full of concentrates. The lower end of the bin hoppers is on the same level with the water-tight floor and the openings in the hoppers are 16 in. square. Arc gates, which can be made practically water-tight by means of tightening levers, are fastened to the hoppers and the bins are unloaded through these gates when full.

All slime-table lead-iron concentrates are shoveled out of the settling boxes by hand into mine cars and trammed to railroad cars. The zinc-iron concentrates are also shoveled into mine cars and are trammed to the electrostatic mill. The mine cars containing the zinc-iron concentrates are placed on a platform elevator and raised to the top of the electrostatic-mill bin where they are dumped; this bin holds about 25 cars.

TAILINGS DISPOSAL

The mill tailings are carried, by a system of launders, to a central launder, which carries them to a small sump outside of the mill building. From this sump, they are carried by an inverted siphon, which is a 10-in. concrete pipe, to a launder which empties into the feed well of a 90-ft. Dorr thickener situated on the tailings dump. This thickener removes about 55 per cent. of the water in a clear overflow, which goes into the Jordan River. The thickener spigot goes to either of two 6-in. Wilfley sand pumps, which discharge into a distributing box. From this box, the tailings are carried to the dump and settled in large ponds, the overflows from the ponds going in to the river. No tailings water is returned to the mill. A Teeter box sampler is used for sampling the tailings. The average mill tailings contain about 0.02 oz. gold, 1.1 oz. silver, 1.7 per cent. lead, $3\frac{1}{2}$ per cent. iron, and $5\frac{1}{4}$ per cent. zinc.

ELECTROSTATIC MILL

This mill handles the zinc-iron concentrates from the wet mill and produces zinc concentrates and iron concentrates. The iron concentrates are sent to the company's lead smelter and the zinc concentrates to a zinc smelter.

The zinc-iron concentrates are fed from the receiving bin to a Ruggles-Coles Type A Dryer. The concentrates contain about $12\frac{1}{2}$ per cent. moisture when they enter and must be bone dry and have a temperature of 280° F. when discharged. The dryer has a capacity of 100 tons in 24 hr. and requires about 75 lb. of slack coal per ton of ore dried; it is operated with forced draft. The gases are discharged, through a 45-in. exhaust fan,

into a small brick chamber from which they pass to the atmosphere through a steel stack 30 in. in diameter and 48 ft. high. The dryer discharges into a bucket elevator, which carries the dried material to a distributing box; thence it passes to the screens, about 75 per cent. going to Hummers and 25 per cent. to Type H Newaygos.

Both the Hummer and Newaygo screens are set in two banks, one below the other, with two screening surfaces in each bank. All screening surfaces are 6 ft. long and 6 ft. wide and are set at an angle of about 32° from the horizontal. The top screen in the upper bank is 16-mesh steel-wire cloth with 0.0445-in. square openings and the bottom screen is 40-mesh brass-wire cloth with 0.014-in. square openings. The top screen in the lower bank is 60-mesh brass-wire cloth with 0.007-in. square openings and the bottom screen is 100-mesh brass-wire cloth with 0.0045-in. square openings. The material must be closely sized before going to the Huff electrostatic separators. The 16-mesh screen is used as a scalper. The material that remains on this screen is oversize and is returned to the tube-mill circuit in the wet mill. This oversize amounts to about 2 per cent. of the total electrostatic mill feed. The four sized products from the Hummer screens go to four small bucket elevators, from which they are distributed to the feed hoppers of the electrostatic machines by 2-in. pipes. The products from the Newaygo screens are sent to electrostatic machines by means of 6-in. screw conveyors. The distributing system is so arranged that the number of machines treating any size can be varied as the amount of that size varies.

There are thirty-two Huff machines in the mill; eighteen are remodeled type D and fourteen are type F. Each type F machine consists of a rougher and two finishers combined in one unit. The remodeled type D machines are all separate so that three machines are required to make a unit similar to the Type F unit.

The roughers make rougher zinc concentrates and rougher iron concentrates. The rougher zinc concentrates pass to the zinc finishers and the rougher iron concentrates to the iron finishers. The zinc finishers make a finished zinc product and a mixed product. The iron finishers make finished iron concentrates and a mixed product. The finished concentrates pass to small hopper bins directly under the machines and the two mixed products are combined and returned to the elevators or screw conveyors that feed the roughers. The amount of mixed product returned to the roughers varies from 25 to 40 per cent. of the total rougher feed, depending on the metal contents and character of the zinc-iron concentrates being treated. The finished products are loaded from the small hopper bins into mine cars and trammed to railroad cars. It is essential that the zinc-iron concentrates be absolutely dry and hot enough so that they will not absorb moisture when passing through the mill circuit.

The mechanical power required by the electrostatic machines is very small. The only moving part on the type F machines is a 3-in. feed roller, while the remodeled type D machines have a 1½-in. feed roller on both the roughers and finishers. The electrical energy for the thirty-two machines in the mill is furnished by a small motor-generator set. This consists of a 7½-kw. generator direct-connected to a 5-hp. motor. The current from the generator is stepped up, by a transformer, from 120 volts to the voltage required at the machines, which varies from 18,000 to 22,000. The intensity of current is a very small fraction of an ampere. The high-tension current passes through a rectifier before going to the electrostatic machines and is converted into a unidirectional pulsating current. The motor-generator set would supply current for additional machines.

ANALYSIS OF ELECTROSTATIC MILL HEADS AND OF FINISHED PRODUCTS

	ELECTROSTATIC MILL HEADS	ZINC CONCENTRATES	IRON CONCENTRATES
Gold, ounce.	0.07	0.03	0.12
Silver, ounce.	3.00	1.40	4.50
Copper, per cent.	0.65	0.40	0.98
Lead, per cent.	3.30	1.80	4.90
Insoluble, per cent.	5.60	8.20	2.00
Iron, per cent.	23.00	6.20	35.00
Zinc, per cent.	26.00	49.50	8.00
Sulfur, per cent.	37.50	31.00	43.00

DUST-COLLECTING SYSTEM

The electrostatic machines, and all other machines in the mill that tend to make dust, are connected by pipes to the intake of a 70-in. exhaust fan. The dust laden air from the fan passes first into dust chambers and then into the baghouse. The material collected in the chambers nearest the fan is returned to the dryer and retreated with the original mill heads; that which is collected in the remaining chambers and in the baghouse is not retreated. Its metal contents are about the same as those of the mill heads. The dust loss, including that which passes up the dryer stack, amounts to about 6 per cent. of the original electrostatic-mill heads. The bags used in the baghouse are 12 in. in diameter and 16 ft. long and are made of a medium-weight cotton cloth.

LIMITATIONS OF THE HUFF MACHINES

The mineralogical character of the sphalerite in the ores milled varies greatly. At times, it is largely "black jack", which contains from 3 to 7 per cent. iron chemically combined with the zinc. Then the "blackjack" will almost disappear and the zinc mineral is mostly of a light brown or yellow color, almost free from iron. Occasionally the ore contains considerable pyrite, which has become somewhat oxidized and this oxida-

tion affects its electrical conductivity. When the pyrite is unaltered and the sphalerite is mostly of the light-colored variety, a clean separation of the two minerals can be made without much difficulty. When considerable "blackjack" zinc is present, together with partly oxidized pyrite, it is not possible to make a clean separation because, to repel the partly oxidized pyrite, a higher voltage is required, or the adjustable electrode must be set close to the stream of ore, and either of these adjustments will cause the "blackjack" zinc to be repelled along with the iron. When much "blackjack" is present and the pyrite is not oxidized, it is possible to make a good zinc product but the iron product is usually high in zinc; this, of course, results in a low zinc recovery.

The -100-mesh size is more difficult to separate into commercial products than the three coarser sizes because it contains most of the slimes in the mill feed. About 33 per cent. of the -100-mesh size will pass a 200-mesh screen and contains considerable impalpable dust. The dust builds up on the slides, or toboggans, of the machines and then falls in lumps. It also sticks to the movable electrodes and interferes with the discharge of particles that are repelled. The 200-mesh material can be separated in a fairly satisfactory manner if all of the dust is removed.

The galena and chalcopyrite in the electrostatic-mill feed are usually repelled together with the pyrite if unaltered. Usually about 75 per cent. of these minerals go into the iron concentrates and they carry along an equal percentage of the gold and silver.

RECOVERIES IN WET MILL AND ELECTROSTATIC MILL

The wet mill recovers about 86 per cent. of the lead in the crude ore and an additional 5 per cent. is recovered in the electrostatic-mill iron product. The silver and gold recoveries in the two mills average about 87 per cent. The zinc recovered in the electrostatic mill is about 33 per cent. of the total zinc in the crude ore. About 40 per cent. of the zinc in the crude ore goes into the lead-iron concentrates from the wet mill and the iron concentrates from the electrostatic mill; the remainder is lost in the tailings.

FLOTATION MILL

About a year ago, the company decided to build a pilot flotation mill to prove out laboratory tests, which had indicated that a considerably greater percentage of the zinc could be recovered by flotation methods than was possible by gravity concentration combined with electrostatic treatment. The laboratory tests also indicated that lead-zinc ores could be handled, which were not amenable to gravity concentration or to electrostatic separation on account of the intimate association of the minerals.

A small mill, adjacent to the main concentrator, which was formerly used for concentrating custom ores, was remodeled into a 20-ton flotation unit and the capacity of this unit was later increased to 50 tons per day. Various ores have been handled in this mill and the results obtained have generally confirmed the laboratory test results.

In this mill, the crude ore is crushed dry to $\frac{1}{2}$ in. by a Blake crusher and a set of 30 by 12-in. rolls and sent to the fine-ore bin, which has a capacity of about 125 tons. From this bin, the ore is fed by a plunger feeder into the boot of a bucket elevator which discharges into a 5 by 3-ft. trommel fitted with 4-mesh steel-wire screens. Water is added in the boot of the elevator. The oversize from the trommel goes to a set of 30 by 12-in. rolls and then back to the elevator. The trommel undersize goes to a 6 ft. by 16-in. Hardinge ball mill, which is operated in closed circuit with a 36-in. Akins classifier. The classifier overflow is the feed to the flotation machines and contains about 20 per cent. solids of which about 65 per cent. will pass a 200-mesh screen and 100 per cent. will pass a 65-mesh screen. Some ores require finer crushing to liberate all of the minerals.

The ball charge used in the Hardinge mill is made up of $2\frac{1}{2}$, 2, and $1\frac{1}{2}$ -in. cast-iron balls and weighs about 7500 lb. The $2\frac{1}{2}$ -in. balls are fed into the mill daily, to keep the charge constant in weight. The ball consumption averages about 1.7 lb. per ton of ore ground. The ball-mill lining is "Titanite," which has a life of approximately 8 months.

The following oils and reagents are added at the ball-mill: sodium sulfite, Barrett No. 4 or similar oil and steam-distilled pine oil. On some ores, sodium sulfide and sodium silicate are also used.

The Akins classifier overflow is pumped by a 2-in. Wilfley sand pump to a small surge tank of about 250 gal. capacity. From this surge tank, the pulp is sent to the head cell of the flotation circuit. The flotation machines used are Minerals Separation standard type, Minerals Separation subaeration type, and one 6-ft. Fagergren. The lead is floated first in an eight-cell, 18-in. M.S. subaeration machine. A lead middling is cut off on the last two to four cells of the lead circuit and returned to the head cell. The lead tailings go to the zinc circuit, which consists of one six-cell, 18-in. M.S. standard machine and one eight-cell 18-in. M.S. subaeration machine. The zinc concentrates are taken off at the standard cells and the subaeration cells are used for making zinc middlings, which are returned to the head of the zinc circuit. Cone tanks are used for thickening and conditioning in the zinc circuit and these are placed between the standard cells and the subaeration cells. The zinc tailings go to the Fagergren machine, which makes iron concentrates and tailings. The Fagergren tailings go to a six-cell, 12-in. M.S. subaeration machine, which also makes iron concentrates and tailings. These tailings are sent

to a Wilfley table, which is used merely as a pilot table. None of the concentrates are cleaned.

The reagents and oils used in the lead circuit are as follows: Steam-distilled pine oil, Barrett No. 4 or similar oil and potassium xanthate. On some ores, soda ash is used in the lead circuit. The following are used in the zinc circuit: pine oil, Barrett No. 4 or similar oil, hardwood creosote, potassium xanthate and copper sulfate. In the iron circuit, sodium sulfide is added; and on some ores, a small amount of pine oil and Barrett No. 4.

The flotation products are thickened and filtered in accordance with standard practice. One three-disk 6-ft. American filter is used for filtering all three products. Water-tight partitions are placed in the filter tank and each disk handles a separate product.

The ores handled in the flotation mill have varied widely in mineralogical and physical character and in their metal contents. These variations have, of course, caused corresponding variations in the grade of the products and in the metal recoveries. All metal recoveries have been satisfactory, except in the case of ores that contained large percentages of oxidized mineral.

Effect of Cyanogen Compounds on Floatability of Pure Sulfide Minerals.—I*

BY E. L. TUCKER† AND R. E. HEAD,‡ SALT LAKE CITY, UTAH

(Salt Lake City Meeting, September, 1925)

IN THE metallurgy of precious metals, it has been standard practice for years to use cyanogen compounds, so it was but natural that early investigators in the field of flotation should consider these compounds as possible flotation reagents. In Australian Patent 9508, of 1913, alkali cyanides were described as suitable reagents for the separation of heavy sulfide minerals, the reagents being employed either in an alkaline or neutral circuit. In U. S. Patent 1236501, of 1917, to John M. Tibbet, the use of cyanide in conjunction with soda ash or lime is described. One of the claims of this patent reads, "An improvement in the cyanide process for the treatment of ores comprising, mixing the ore with cyanide solution and oil and alkali: emulsifying the oil in the presence of the ore, the alkali and the cyanide solution, floating a portion of the values in the pulp by producing gas bubbles in the mixture and removing the values floated." More recently, Sheridan and Griswold, in U. S. Patents 1421585 and 1427235, describe a somewhat similar process and have successfully introduced it in the mill of the Timber Butte Milling Co. U. S. Patent 1429544, of 1922, to Stevens, describes the use of double cyanides of copper, zinc, and lead.

The success of cyanide as a reagent in the differential flotation of lead and zinc sulfides in highly complex ores is proof that these patents have a solid foundation. Although the technique of their application to particular ores has been worked out in many cases, no one, so far as is known, has attempted to describe the nature of the action of the cyanide or to determine the ideal conditions for its application. It was the purpose of the present investigation to gather information on these points. Naturally this would have been an exceedingly ambitious program had the attempt been made to study the effect of cyanide

* Investigation Conducted Under Coöperative Agreement Between the Bureau of Mines and the American Cyanamid Co. at the Intermountain Experiment Station.

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† Technical Department, American Cyanamid Co.

‡ Microscopist, Bureau of Mines.

reagents on all the ores that have been found amenable to the cyanide-flotation treatment. For this reason, the study was limited to the effect of the reagents on pure minerals; consequently the title of this paper adequately describes the more modest scope of the work. Although much of the practical value is sacrificed by using only pure minerals, this procedure eliminates many variables that would be difficult to control, and has made it possible to observe phenomena that appear of value in the study of differential flotation. While this paper covers but one phase of the subject, the authors realize that many interesting side lines might be followed and establish additional facts of practical and scientific value.

MINERALS USED

The galena and sphalerite used were carefully picked from jig concentrates from Missouri; the pyrite, a massive variety, was secured from the Ward Mineral Co. Each mineral was crushed in stages through rolls to secure a uniform product, all of which passed a 200-mesh screen. In some instances, it was necessary to crush either on the backing board or in a disk pulverizer to secure the desired fineness. All tramp iron was removed by a large magnet, to insure that the final sample was as nearly pure mineral as could be obtained. The following analyses show the general grade of the finished product:

	FE PER CENT.	PB PER CENT.	ZN PER CENT.	CAO PER CENT.	MGO PER CENT.	S PER CENT.	INSOL. PER CENT.
Pyrite....	43.18	0.92	0.30	47.44	7.61
Galena....	1.07	79 23	0 13	1.86
Sphalerite	0 51	0 46	63 50	3.16

EXPERIMENTAL PROCEDURE

A small 50-gm., mechanically agitated flotation machine¹ designed by L. K. Jacobsen and J. F. Gates, of the Metallurgical Research Department of the University of Utah, in coöperation with the Bureau of Mines, was used throughout the tests. Though small, this machine compared favorably with the larger type of machine and gave very consistent results. The data presented were checked by duplicate, and in some cases triplicate, runs and the maximum error was under 5 per cent. By using this type of machine one is able to make a large number of tests without depending on assays, as a drying and weighing of the concentrates gives the relative recovery of mineral under set conditions. The oils used were dropped from a pinpoint, and the weight of the drops was carefully determined beforehand. Blank runs were made on each mineral, using distilled water alone.

¹ *Eng. & Min. Jnl.-Pr.* (1925) **119**, 771.

To wet the mineral thoroughly each 50-gm. charge was agitated in a small jar at 1 to 1 dilution for a few minutes before proceeding with the flotation. Whenever addition reagents were used, they were added dry to the jar and were agitated with the pulp so as to insure thorough mixing.

Effect of Soda Ash and Lime Alkalinity on Floatability of Pure Minerals

Cyanogen compounds may be used only in neutral or alkaline circuits, and as it is difficult, if not impossible, to maintain exact neutrality in

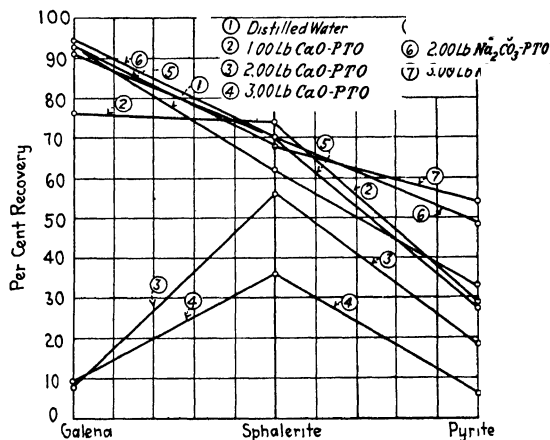


FIG. 1.—EFFECT OF LIME AND SODIUM CARBONATE ON FLOTATION OF SULFIDE MINERALS.

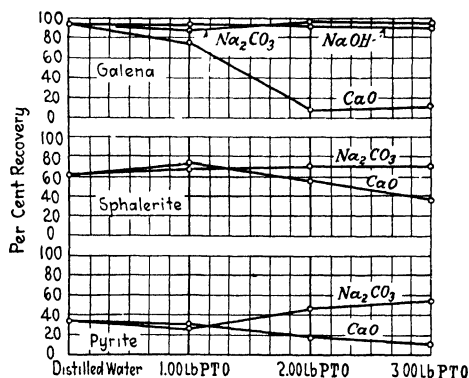


FIG. 2.—EFFECT OF ALKALINE CONCENTRATION ON FLOTATION OF SULFIDE MINERALS.

such circuits, the alkaline circuit must be maintained in practice. In the ordinary cyanidation treatment of precious metals, alkalinity is maintained by the use of lime; consequently, at first, it may seem surprising that flotation practice has adopted the much more expensive sodium-carbonate circuit. That this choice rests on solid foundation is shown by Figs. 1 and 2; the floatability of the galena is greatly lessened by lime and slightly increased by soda ash. This effect is due to the calcium ion,

as was shown by further experiments which need not be detailed here. Soluble calcium salts, the chloride for example, are equally effective in retarding the flotation of galena. The function of the sodium carbonate in the cyanide flotation is, therefore, to free the circuit water from soluble calcium salts and to neutralize acidic constituents of the ore. In addition, sodium carbonate has been found, by other workers, to be a somewhat effective reagent for the differential flotation of lead from copper and zinc even when used alone.

Effect of Sodium Cyanide in Presence of Sodium Carbonate and Lime

Fig. 3 shows the effect of sodium cyanide on the behavior of galena, sphalerite, and pyrite in solutions made alkaline with lime and sodium carbonate. Sodium cyanide alone has little effect on the pure minerals;

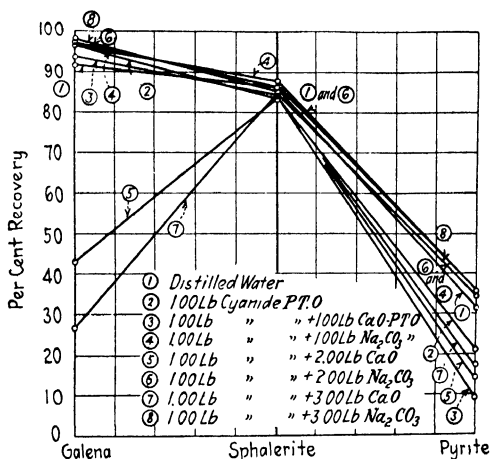


FIG. 3.—EFFECT OF CYANIDE ON FLOTATION OF SULFIDE MINERALS.

probably in those cases where sodium cyanide alone is found effective in practice, it is because of the combined action of the cyanide and some soluble constituent of the ore.

Further discussion of this action of cyanide will be taken up later. The more usual method of application of the cyanide is in combination with a cheap heavy metal salt, such as zinc sulfate, as is shown below.

Effect of Zinc Cyanide Mixture in Presence of Sodium Carbonate and Lime

Fig. 4 shows the advantage to be gained by using a combination of zinc sulfate and sodium cyanide; this gives ideal conditions for the separation of galena from sphalerite and pyrite. The proportioning of the reagents used is somewhat arbitrary, the relation being such that no free cyanide exists and one half or more of the cyanide is precipitated as the insoluble zinc cyanide. The question may be raised whether this depres-

sion is caused by the precipitated zinc cyanide or by the soluble double cyanide. With sphalerite, whose normal rate of flotation is 62 per cent. in distilled water, the addition of 2 lb. of sodium cyanide and 1 lb. of zinc sulfate gave a recovery of 63 per cent., and with 4 lb. of cyanide and 2 lb.

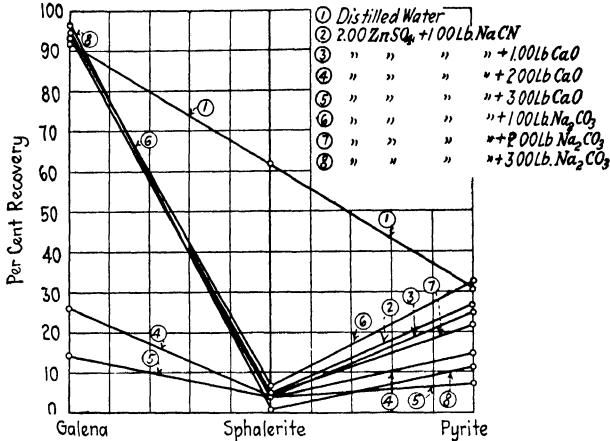


FIG. 4.—EFFECT OF ZINC SULFATE AND CYANIDE ON FLOTATION OF SULFIDE MINERALS.

of zinc sulfate a decrease to 49 per cent. In the presence of zinc ferrocyanide, made by adding 1 lb. of sodium ferrocyanide and 2 lb. of zinc sulfate, the recovery is only 56 per cent. No attempt will be made at

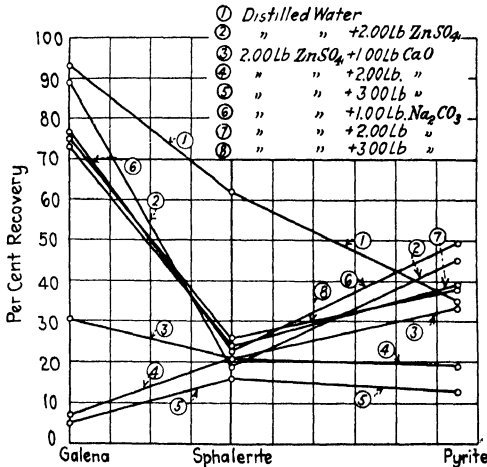


FIG. 5.—EFFECT OF ZINC SULFATE ON FLOTATION OF SULFIDE MINERALS.

this time to go further into the subject of properly proportioning the cyanide and zinc sulfate, the evidence being sufficiently clear that the zinc sulfate and cyanide should be substantially in the proportion indicated for the formation of the compounds $\text{Zn}(\text{CN})_2$.

The depressing action of the zinc-cyanide mixture is not caused entirely by the zinc sulfate, as may be seen by comparing the action of zinc sulfate alone in Figs. 5 and 6.

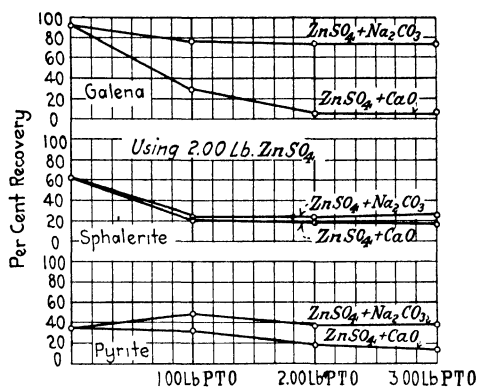


FIG. 6.—EFFECT OF ZINC SULFATE WITH LIME AND SODA ASH.

Effect of Zinc Sulfate in Presence of Sodium Carbonate and Lime

Figs. 5 and 6 show the action of zinc sulfate on galena, sphalerite, and pyrite when used alone and when used in the presence of lime and sodium carbonate. From this series of experiments, it appears that although zinc sulfate alone is a depressant for sphalerite, the effect is

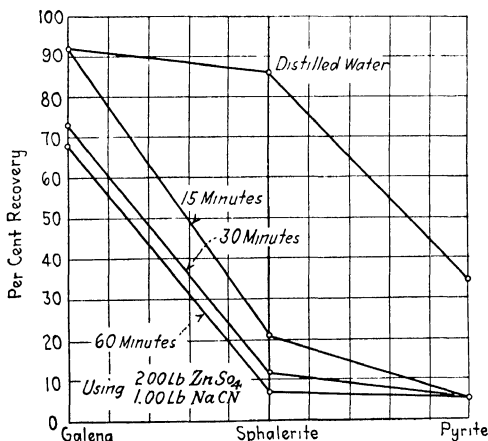


FIG. 7.—FLOATABILITY OF SULFIDES WITH DIFFERENT PERIODS OF CONTACT.

greatly accentuated by the addition of the cyanide. Further advantage is gained by the use of the cyanide in that the depression of the galena produced by the zinc sulfate alone is not observed when cyanide is present. Obviously, then, the zinc sulfate and sodium cyanide combination is ideal for the commercial separation of galena from sphalerite and pyrite.

Time of Contact

Fig. 7 shows the effect of time on the relative floatability of the three minerals. Increasing the time element appears to increase the depressing action on the sphalerite. The usual method of adding the mixture of zinc sulfate and cyanide at the ball mill ordinarily allows for a sufficient time of contact.

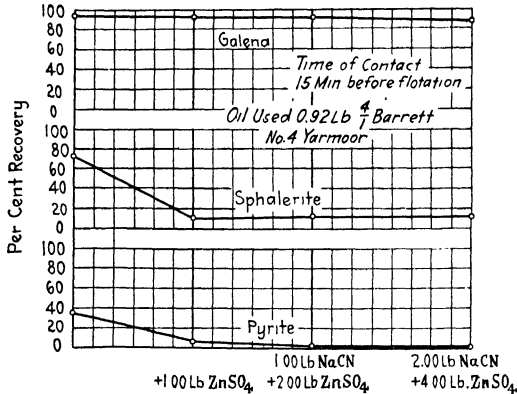


FIG. 8.—EFFECT OF CONCENTRATION OF ZINC SULFATE AND CYANIDE.

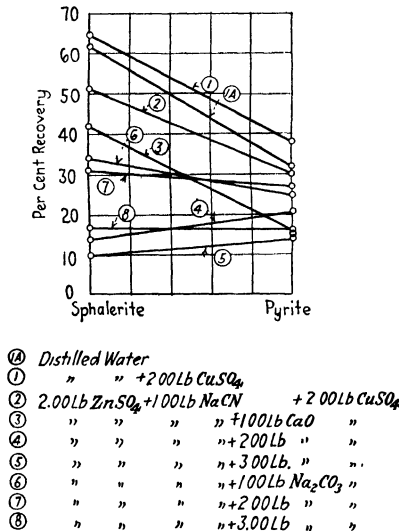


FIG. 9.—EFFECT OF COPPER SULFATE ON FLOTATION OF SPHALERITE AND PYRITE.

Effect of Concentration of Zinc Sulfate and Cyanide Mixture

Fig. 8 shows the effect of zinc sulfate and cyanide over the range of concentration covered. The flotation of the galena and sphalerite was about the same at all concentrations. Increasing the concentration still further inhibited the flotation of the pyrite.

Effect of Copper Sulfate on Sphalerite and Pyrite Sickened by Zinc Cyanide

The use of copper sulfate for promoting the flotation of sphalerite has been standard practice for years. The following series of experiments were run to show that the sphalerite, deadened by the cyanide mixture, could be reactivated by the use of copper sulfate. Larger amounts of oil will be necessary to raise the deadened sphalerite to its normal rate of flotation.

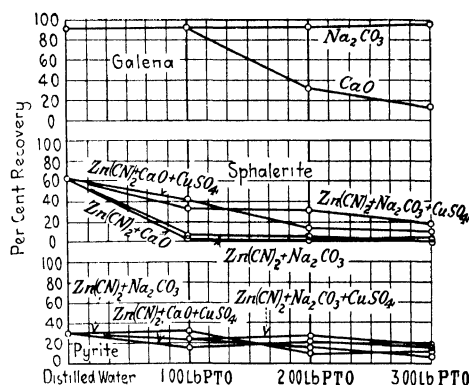


FIG. 10.—EFFECT OF ALKALINE CONCENTRATION, USING ZINC SULFATE AND CYANIDE WITH AND WITHOUT COPPER SULFATE.

Figs. 9 and 10 show the effect of adding the copper sulfate to the previously sickened sphalerite and pyrite; the zinc is reactivated, but the pyrite is not, thus allowing a clean separation of the sphalerite and pyrite to be made.

Table 1 shows the results of all the investigations that have been described.

Effect of Each Reagent and Combination

Our conclusions concerning the effect of each reagent and each combination of reagents upon the several minerals included in this study are as follows, 1 lb. of cyanide and 2 lb. of zinc sulfate with varying amounts of soda ash or lime being used in each case, unless otherwise specified:

Galena

1. Under the conditions of the experiment, the floatability of galena in distilled water alone is 92.0 per cent.

2. *Effect of Lime.*—Floatability is decreased to 76 per cent. by 1 lb. of lime, and to 6 and 8 per cent. by 2 and 3 lb. respectively.

3. *Effect of Soda Ash.*—Floatability of galena appears to be unchanged by amounts of soda ash up to 3 lb. per ton.

TABLE 1.—*Data Obtained from the Experiments*

Fig. No.	Line No.	Reagents 0.92 Lb. Barrett #4 Yarmour's						Mineral Minus 200 Mesh		
		CaO	Na- CO ₃	NaCN	ZnSO ₄	CuSO ₄		Galena	Sphal- erite	Pyrite
1	1						Distilled water	92	62	33
	2	1.0						76	74	30
	3	2.0						6	56	18
	4	3.0						8	36	7
	5		1.0					92	70	28
	6		2.0					93	70	48
	7		3.0					92	68	55
3	1						Distilled water	92	87	32
	2			1.0				96	82	21
	3	1.0		1.0				93	83	8
	5	2.0		1.0				43	82	15
	7	3.0		1.0				32	83	18
	4		1.0	1.0				96	88	35
	6		2.0	1.0				97	87	36
4	8		3.0	1.0				98	85	35
	1						Distilled water	92	62	30
	2			1.0	2.0			93	5	27
	3	1.0		1.0	2.0			94	4	25
	4	2.0		1.0	2.0			26	4	15
	5	3.0		1.0	2.0			15	5	8
	6		1.0	1.0	2.0			94	7	34
	7		2.0	1.0	2.0			94	5	21
9	8		3.0	1.0	2.0			96	2	12
	1A						Distilled water		62	32
	1					2.0			65	38
	2			1.0	2.0	2.0			51	30
	3	1.0		1.0	2.0	2.0			42	16
	4	2.0		1.0	2.0	2.0			14	21
	5	3.0		1.0	2.0	2.0			10	14
	6		1.0	1.0	2.0	2.0			34	24
5	7		2.0	1.0	2.0	2.0			31	16
	8		3.0	1.0	2.0	2.0			17	16
	1						Distilled water	93	62	35
	2				2.0			90	20	45
	3	1.0			2.0			30	21	33
	4	2.0			2.0			7	19	19
	5	3.0			2.0			5	16	13
	6		1.0		2.0			77	23	49
	7		2.0		2.0			75	24	39
	8		3.0		2.0			73	26	38

4. *Effect of Cyanide Alone.*—Floatability is increased to 96.0 per cent. with 1 pound.

Effect of Cyanide and Soda Ash.—Same as for cyanide.

Effect of Cyanide and Lime.—With 1 lb. of lime, same as for distilled water; rapid decrease of floatability with more lime, that is, to 43 per cent. with 2 lb. and to 32 per cent. with 3 lb.

5. *Effect of Zinc Sulfate.*—Floatability of galena is slightly decreased by 2 lb. per ton of ore.

Effect of Zinc Sulfate and Soda Ash.—With 2 lb. of zinc sulfate the flotation of galena is decreased to 77 per cent. with 1 lb. of soda ash, and to 75 per cent. with 2 lb. and to 73 per cent. with 3 lb.

Effect of Zinc Sulfate and Lime.—Rapid decrease, 30–7–5 per cent. with 1, 2, and 3 lb. of lime.

6. *Effect of Cyanide and Zinc Sulfate Alone.*—Same as that of distilled water.

Effect of Cyanide and Zinc Sulfate and Soda Ash.—Possible slight increase up to 3 lb. of soda ash.

Effect of Cyanide and Zinc Sulfate and Lime.—There is little effect with 1 lb. of lime; but rapid decrease with 2 and 3 lb.

7. *Effect of High Zinc Cyanide Concentrations.*—Increasing the concentration gives a slight depression.

8. *Effect of Time of Contact.*—Moderate depression with long periods of contact.

Sphalerite

1. The floatability of the sphalerite used varied from 62 to 87 per cent. depending on the amount of fine slimes in the minus 200-mesh product.

2. *Effect of Lime.*—The effect of lime is, in general, to decrease the floatability at high concentrations; 1 lb. addition gave an acceleration from 62–74 per cent., but 2 and 3 lb. decreased it to 56 and 36 per cent., respectively.

3. *Effect of Soda Ash.*—None.

4. *Effect of Cyanide Alone.*—Very slight decrease to 82 per cent. using distilled water floatability as 87 per cent.

Effect of Cyanide and Soda.—No change.

Effect of Cyanide and Lime.—Same as for cyanide alone; lime did not decrease the floatability in the presence of cyanide.

5. *Effect of Zinc Sulfate.*—Decreases the floatability from 62 to 20 per cent.

Effect of Zinc Sulfate and Soda Ash.—Decrease to 23 per cent. with 1 lb. addition, and 24 and 26 per cent. with 2 and 3 lb. respectively.

Effect of Zinc Sulfate and Lime.—Gradual decrease with increasing concentration from 62 per cent. to 21–19 and 16 per cent.

6. *Effect of Cyanide and Zinc Sulfate Alone.*—Reduction in the rate of floatability from 62 to 5 per cent.

Effect of Cyanide and Zinc Sulfate and Soda Ash.—Decreases from 62 to 7–5–2 per cent. with increased soda ash concentration.

Effect of Cyanide and Zinc Sulfate and Lime.—Decrease to about 4 per cent. produced at all concentrations of lime.

7. *Effect of High Zinc Cyanide Concentration.*—No change in rate of floatability over that of lower concentrations.

8. *Effect of Time of Contact.*—Increasing depression on long contact with zinc-cyanide mixtures.

Pyrite

1. The floatability of pyrite in distilled water averaged 32 per cent.

2. *Effect of Lime.*—Lime alone gives a rapid decrease in the rate of floatability with increased concentration, the rates being 30–18–7 per cent. with 1, 2, and 3 lb. respectively.

3. *Effect of Soda Ash.*—Soda ash gives an increasing rate of floatability 28–48–55 per cent., with 1, 2, and 3 lb. of soda ash.

4. *Effect of Cyanide Alone.*—The rate of floatability decreases to 21 per cent. with 1 lb. of cyanide.

Effect of Cyanide and Soda Ash.—Rate of floatability changed from 32 per cent. to 34–21–12 per cent. with 1, 2, and 3 lb. respectively, of soda ash.

Effect of Cyanide and Lime.—Decrease to 8–15–18 per cent. with 1, 2, and 3 lb. of lime.

5. *Effect of Zinc Sulfate Alone.*—Flotation is increased to 45 per cent. with 2 lb. of zinc sulfate.

Effect of Zinc Sulfate and Soda Ash.—Flotation is increased over that in distilled water but decreased with increased concentration—49–39–38 per cent. with 1, 2, and 3 lb. respectively of soda ash.

Effect of Zinc Sulfate and Lime.—Decreases with increased lime concentration (33–19–13 per cent.), but not as low as with lime alone.

6. *Effect of Cyanide and Zinc Sulfate Alone.*—Gives a slight decrease in the rate of floatability.

Effect of Cyanide and Zinc Sulfate and Soda Ash.—Decreased floatability with increased concentration of soda ash—34–31–12 per cent. respectively.

Effect of Cyanide and Zinc Sulfate and Lime.—Rapid decrease to 25–15–8 per cent. with 1, 2, and 3 lb. of lime.

7. *Effect of High Zinc-cyanide Concentration.*—Rapid decrease with increasing concentration.

8. *Effect of Time of Contact.*—No change.

Having thus confirmed the beneficial effect of the zinc-cyanide combination in the separation of galena, sphalerite, and pyrite, it is of

interest to interpret its action as shown by microscopic study of the mineral surfaces themselves.

MICROSCOPIC INVESTIGATIONS

After preliminary investigation, it was found that the zinc-cyanide mixture appeared to have changed the surfaces of the pure minerals in some manner that apparently had a marked effect on their floatability. As the surface effects on the three minerals were unlike, it seemed probable that selective filming might account for the change in the rate of floatability. The following method of procedure was adopted in studying this filming action, the metallurgical microscope being used for the examination and photographing of the mineral surfaces.

A piece of freshly broken sulfide mineral, about $\frac{5}{16}$ in. long, that showed a clean, plane face was used for each test. One-half of the surface



FIG. 11.—IMMERSION LINE OF GALENA.

of the mineral to be examined was coated with melted paraffin to prevent solution contact. The mineral particle was tied to the impeller shaft of a small M-S type machine and agitated in a solution containing zinc-cyanide mixture for 20 min. The mineral was taken from the machine, washed thoroughly with distilled water, and the paraffin removed. The dividing line between the surface in contact with the solution and that covered with paraffin could then be easily seen and examined microscopically. Figs. 11, 12, and 13 show the mineral particles after removal from the machine; the dividing line is visible on close examination; Figs. 14, 15, and 16 are photomicrographs of a section of the dividing line. In each case blank tests were run using distilled water alone, but in no instance did the mineral particles show any

indication of surface change or oxidation under the conditions described. It appears that the galena particle was the least affected by this treatment, the sphalerite next, and the pyrite most.

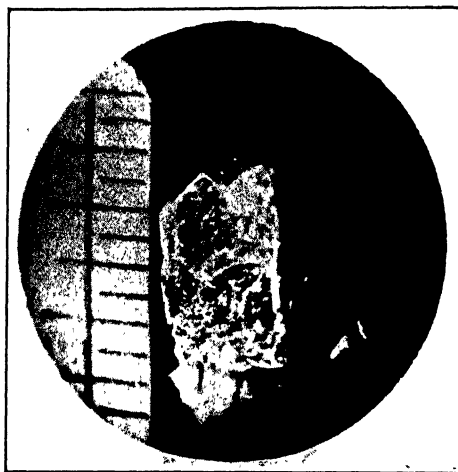


FIG. 12.—IMMERSION LINE OF SPHALERITE.

In Fig. 13, which shows the pyrite grain, the surface effect is apparent to the unaided eye; there is a sharp well-defined line of demarkation between the portion of the grain exposed to the solution and that which



FIG. 13.—IMMERSION LINE OF PYRITE.

had been protected by the paraffin film. This surface effect is exceedingly clear in Fig. 16. The portion that had been exposed to the solution is non-reflective of light, while that which was paraffined possesses the full reflec-

tive characteristics of a perfectly polished surface. At a magnification of 145 diameters, the effect appears due to the quite uniform deposition of salts over the exposed area; also, there was an impression that the surface had been attacked; this latter condition was corroborated by the amount of cyanide consumed. To investigate further the etching or surface alteration, the area in question was vigorously rubbed with a piece of soft lens paper, which removed the absorbed salts. The area



FIG. 14.—PHOTOMICROGRAPH OF IMMERSION LINE OF GALENA.

was examined under the same conditions of light and magnification as before. At this magnification (X145), the area that had been filmed and apparently etched showed nothing distinctive in the way of decreased luster when compared with the untreated portion of the pyrite, but it was evident that a very slight or incipient development of minute pits had resulted. At a higher magnification (X235) this difference between the two surfaces can be more clearly seen, but the evidences of surface dis-

solution are faint; most of the effect is due to a surface film or deposit of adsorbed salts.

In sphalerite (Figs. 12 and 15), the eye can detect a difference between the exposed and unexposed portions of the particle. The distribution of adsorbed salts, as shown in the right-hand area of Fig. 15, is not nearly so uniform as in the case of the pyrite. Portions of the exposed surface show no deposited salts, and the adsorption may, in a general way, be described

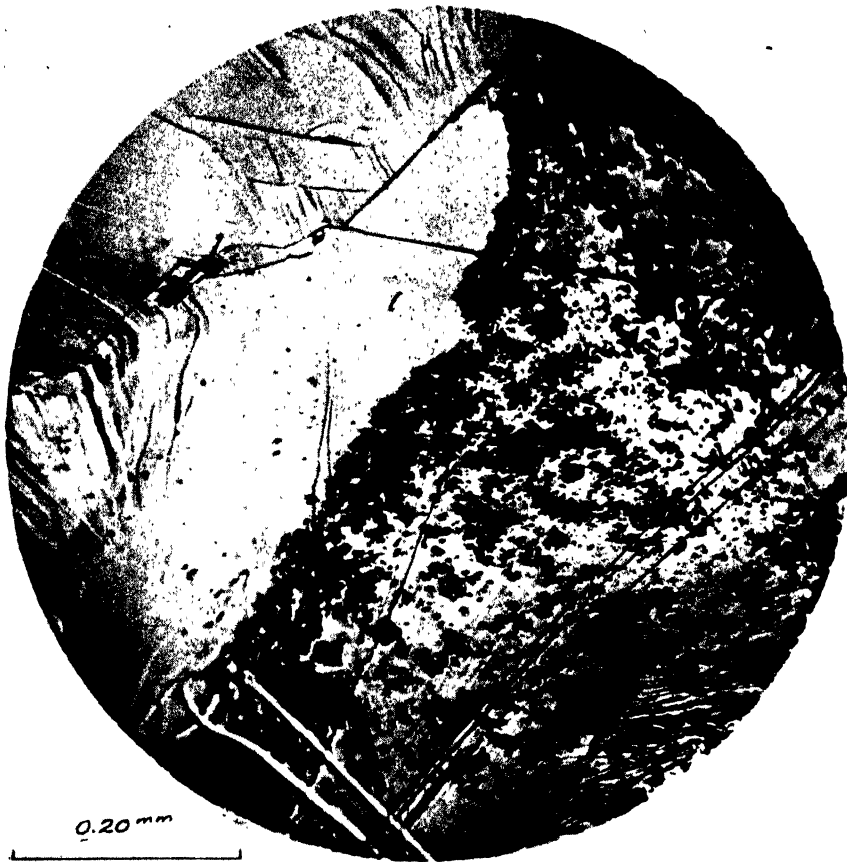


FIG. 15.—PHOTOMICROGRAPH OF IMMERSION LINE OF SPHALERITE.

as distinctly scattered or to consist of aggregates that might be expected to build up or spread out and cover the entire surface with a longer period of contact. In speaking of the distribution of the salts deposited being scattered, it is pointed out that this observation is made from a standpoint of microscopic distances, which can be better appreciated by bearing in mind that the actual diameter of the area shown in Fig. 15 is slightly more than 0.60 mm.

The effect of the zinc-cyanide mixture on the galena was not as apparent on the sphalerite and pyrite. In so far as could be determined by the unaided eye, there was no material change in the appearance of the surface. Fig. 14 shows a section of the dividing line under the same conditions as that of the sphalerite and pyrite, and the adsorption may be considered negligible. This specimen was examined at 750 diameters magnification and no material change could be noticed.



FIG. 16.—PHOTOMICROGRAPH OF IMMERSION LINE OF PYRITE.

The facts noted in this report regarding observations made under the microscope should be considered as results of a preliminary investigation, as much additional experimentation will be necessary to confirm some of the conclusions. Under the conditions described, however, the evidence indicates that the three sulfides (galena, sphalerite, and pyrite) are effected to a gradational extent that is clearly visible under the microscope, and which would seemingly account for the different rates of

floatability obtained by the use of cyanogen compounds with other reagents in a flotation circuit.

Microscopic examination has established the fact that certain reagents used in the flotation cell result in the alteration of the mineral surfaces as shown by Figs. 14, 15, and 16. That these artificial alterations materially change the normal floatability constants of the minerals, as established under standard conditions, is shown by the tabulations of the experimental work.

The results obtained in the present investigation suggest that the selective production of films on minerals is an important factor for consideration in the development of controlled differential flotation of all sulfide minerals, and appears worthy of further research and experimentation.

Briefly summarized, the experimental work indicates that the practice of using cyanide in combination with zinc sulfate rests upon solid foundation. This combination gives the most effective depression of sphalerite and pyrite without appreciably inhibiting the flotation of galena, thus allowing a clean separation of the three minerals to be made. It is believed that further research along the lines of selective filming, which is now in progress, will result in data of much value in connection with the elimination of pyrite from concentrates composed of copper-sulfide minerals in addition to those of lead and zinc.

DISCUSSION

B. STEVENS, Temascaltepec, Mexico (written discussion).—Reference is made to the writer's patent as though it were subsequent to those of Sheridan and Griswold. The dates of application are respectively as follows:

March 8, 1920, serial No. 364033, patent No. 1429544

Jan. 13, 1921, serial No. 437030, patent No. 1421585

Jan. 10, 1922, serial No. 528277, patent No. 1427235

The work done by the authors is of the kind that is needed but the observation that cyanide alone does not affect flotation needs further investigation for it is contrary to general experience, and pure solutions are uncommon.

In 1917, experiments conducted by Geo. B. Hinton on the ores of the Rincon Mine, Mexico, showed that a satisfactory flotation of the silver minerals (mainly pyrargyrite) could be made in water, while there was practically no flotation in cyanide solution. The writer thought it probable that inhibition was due to the dissolving action of the cyanide, which directly or indirectly prevented an oil film from being formed on the surface of the mineral. Working on this theory, in 1918, the writer used sodium-cyanide solution for the differential flotation of chalcopyrite and molybdenite at the Nogales, Ariz., mill of the Lower California

Metals Co. The mill, which was of 100 tons daily capacity, worked successfully on this process until the price of molybdenum rendered it unprofitable. A cyanide solution of about 0.1 per cent. was used and the chalcopyrite was afterwards floated by adding sulfuric acid.

Experiments with cyanide were then (1918) made with other ores, notably the galena-blende-chalcopyrite ores of the Duquesne and Washington Camp mines of Arizona; it was possible to separate the galena from the other minerals but not the chalcopyrite from the blende. Later the writer used metallic cyanide salts, because, in the cyanide process, such salts are known to have an action on some and not on other metals. This idea, being supported by experimental work, resulted in the writer's patent application of March 8, 1920, which was sought as a basic protection for the use of metallic cyanides and similar substances.

The use of the electrochemical series in this connection is obvious, but the series for metallic sulfides is different from the better known one given in the textbooks which are only applicable to the elemental metals. The series for the simple sulfides of the metals is given by R. C. Wells.² Inhibition of flotation may be caused directly by chemical activity between the surface and the solution or by the precipitation, on the surface, of some insoluble substance resulting from the chemical action. It might be theoretically interesting to know which of these produces inhibition in the present case but this knowledge is of no practical importance, because a precipitate from a solution on a surface is always due to the chemical action of the solution on that surface, and most of the simple metallic cyanides are insoluble.

It is known that many minerals can be floated in metallurgical cyanide solution, e.g. tetrahedrite and the allied silver-bearing ores; flotation of this kind is being practiced at the cyanide mill of the Premier mine in Northern British Columbia. These minerals are almost insoluble in cyanide solution and their floatability indicates that inhibition of the kind investigated is due to the cyanide in the solutions rather than to the lime.

² The Fractional Precipitation of Some Ore-forming Compounds at Moderate Temperatures. U. S. Geol. Surv. *Bull.* No. 609.

Effect of Cyanogen Compounds on the Floatability of Pure Sulfide Minerals.—II*

BY E. L. TUCKER†, J. F. GATES† AND R. E. HEAD‡

PREVIOUS investigations of E. L. Tucker and R. E. Head¹ related in particular to the effect of cyanogen compounds on galena, sphalerite, and pyrite, and their behavior in the presence of such compounds. The present contribution deals with the floatability of the copper minerals and of pyrite.

All experiments were performed on minus 200-mesh material, the method of preparation being the same as that described in the previous article. Flotation tests were made in a small mechanically agitated machine of 50-gm. capacity designed in this laboratory by Gates and Jacobsen.² General Naval Stores pine oil No. 5 and potassium xanthate were used in constant amount in all of the experiments; these agents were selected because of their present wide use in the flotation of copper minerals. Lime additions were varied to secure four final hydrogen ion concentrations, namely, neutral, 0.0005 per cent. CaO, 0.003 per cent. CaO, and 0.02 per cent. CaO. The variation in lime addition was introduced to include the range of alkalinities employed in actual flotation practice.

The minerals employed were the purest obtainable. Their analyses are shown in the following tabulation:

TABLE 1.—*Analyses of Minerals Employed in Experiments*

MINERAL	CU	FE	CAO	S	MGO	INSOL.
Chalcocite.....	77.02	0 49	0 29	21 70	0 08	0 28
Chalcopyrite....	34 50	29.20	0 23	34.10	0 07	1 42
Bornite.....	64.30	9 30	0 12	23.70	0 10	1.95
Pyrite.....	36.90	1.12	49.70	1.51

* Investigation conducted under cooperative agreement between the Bureau of Mines and the American Cyanamid Co. at the Intermountain Experiment Station, University of Utah, Salt Lake City, Utah. Published by permission of the Director, Bureau of Mines, and the American Cyanamid Co.

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‡ Microscopist, Bureau of Mines.

¹ See page 354.

² Development and Operation of a 50-gm. Flotation Machine, *Eng. & Min. Jnl.-Pr.*, vol. 119, 19, 771; also Some Flotation Fundamentals and Their Practical Application, *Bull.* 16, Univ. of Utah, p. 40.

The chalcocite is thus quite pure, containing 77.0 per cent. copper compared with the 79.9 per cent. which is theoretical for Cu_2S . The chalcopyrite is also representative with 34.5 and 29.2 per cent. for the copper and the iron compared with 34.6 and 30.9 per cent., the theoretical for CuFeS_2 . The pyrite contains approximately the theoretical content of iron for FeS_2 .

It is extremely difficult to secure bornite in the pure state. Taking the analyses given in the table above and assuming for bornite the formula Cu_3FeS_3 it was found that the mineral used in the experiments was approximately 60 per cent. bornite and 40 per cent. chalcocite. This was the best grade of bornite that could be supplied by any of the firms dealing in natural mineral collections and any results obtained with it are probably comparable to those obtainable on a mill feed containing bornite.

The data of the experimental work are shown in tabulated form in Table 2 and again graphically in Fig. 1 (page 376).

TABLE 2.—*Summary of Experimental Data*

	Sodium Cyanide Added (Lb. per Ton)	Per Cent. of Mineral Recovered			
		Chalco- pyrite	Chalco- cite	Bornite	Pyrite
Final Solution					
Neutral	None	92 0	92 0	91 7	70 0
	0 5	89 2	79 8	95 2	21 0
	1 0	85 4	87 3	90 5	19 0
Final Solution					
0.0005 per cent. CaO	None	94 3	99 0	92 2	36 0
	0 5	91 4	87 3	95 0	14 0
	1 0	88 1	79 8	90 5	13 0
Final Solution					
0.003 per cent. CaO	None	93 3	60 3	96 0	23 0
	0 5	92 1	97 0	95 0	11 0
	1 0	90 0	96 8	94 5	11 0
Final Solution					
0.02 per cent. CaO	None	91 6	15 2	93 8	2 0
	0 5	91 2	23 7	62 4	1 0
	1 0	89 3	16 6	73 1	2 0

Reagents: 0.612 lb. G. N. S. pine oil No. 5; 0.28 lb. potassium xanthate.

EXPERIMENTAL RESULTS

The experimental results obtained on the respective minerals may be summarized as follows:

Pyrite

The flotation of pyrite can be almost entirely inhibited by proper alkalinity control; however, at any given solution alkalinity a 50 per cent. reduction in the floatability of pyrite may be effected by the use of sodium cyanide in an amount not exceeding 0.50 lb. per ton of mineral. Increasing the cyanide to 1 lb. per ton does not increase the effect. The minimum amount of cyanide necessary for positive depression of pyrite was not determined.

Chalcopyrite

The floatability of chalcopyrite is influenced but little by the degree of alkalinity of the solution. Consequently, a commercial separation of chalcopyrite from pyrite should be obtainable by establishing the solution alkalinity at a point sufficiently high to prevent the flotation of pyrite.

Chalcocite

Chalcocite, although slightly less sensitive to solution alkalinity than pyrite, is nevertheless depressed by increased alkalinity and a commercial separation from pyrite by alkalinity regulation would be made with great difficulty, if at all.

Additions of cyanide as noted under pyrite have little effect on the floatability of chalcocite except at alkalinities which would normally cause depression of chalcocite. At such alkalinities the flotation of chalcocite is increased by the presence of cyanide. The use of cyanide in the commercial separation of chalcocite and pyrite is therefore indicated.

Bornite

Bornite behaves similarly to chalcopyrite and could probably be separated from pyrite by control of solution alkalinity. It has been mentioned that the sample of bornite contained 40 per cent. chalcocite; the difficulty of obtaining uniform, uncontaminated bornite suggests that no two samples would give exactly the same results; however, experiments on specimens obtained from various localities duplicate in a general way the results reported here.

Although it would thus appear possible to separate chalcopyrite from pyrite in the absence of chalcocite by alkalinity control alone, it may nevertheless prove desirable in practice to employ cyanide to insure a more permanent deadening of the pyrite particles. That the deadening effect produced by cyanide is more permanent than that produced by lime alone is shown by the following experiments:

Fifty grams of pyrite were agitated for 15 min. in a 0.05 per cent. solution of lime; the lime solution was then filtered off and the pyrite

floated in distilled water. Fifty-nine per cent. of the mineral floated. This is practically the same as the amount recovered when pyrite was floated in distilled water without previous treatment with lime.

In another experiment, made for the purpose of comparing the inhibitory action of cyanide and lime with that of lime alone, 0.5 lb. of sodium cyanide per ton of mineral was added to the lime solution. Fifty grams of pyrite were agitated in this solution for 15 min.; the solution was then removed by filtering and the pyrite subsequently subjected to flotation in distilled water as in the previous experiment. Only 30 per cent. of the pyrite floated, or approximately but one-half the amount recovered in the froth when lime was used alone.

It is thus evident that the combination of lime and cyanide exerts a more permanent effect on the mineral than lime alone. This apparently indicates that the effect of the cyanide is largely confined to the mineral itself and not to the solution.

It is well known that sodium cyanide is used in conjunction with zinc sulfate in the differential separation of lead and zinc. Indeed it is in many instances impracticable, in lead-zinc differential separation, to depress zinc properly by the use of cyanide alone while the lead concentrate is being removed. The experiments on pure sphalerite reported in our previous paper lend confirmation to this belief. In the case of the separation of the copper minerals from pyrite, zinc sulfate has been found unnecessary. Experiments with the combination of zinc sulfate and cyanide, which are omitted here, gave irregular results that were in no instance better than those secured by use of cyanide alone.

Finally, the effect of small amounts of acid soluble copper minerals on the floatability of the copper sulfides and of pyrite in the presence of cyanide was studied. This was done since it was considered possible that the soluble copper minerals, known to be cyanicides, might consume the cyanide before it had exerted a depressing action upon the pyrite. It was found that the effectiveness of cyanide as a depressant for pyrite was not altered by the presence of 1 per cent. of malachite or cuprite, and it may therefore be assumed that in practice the presence of minor amounts of acid soluble copper minerals may be disregarded.

MICROSCOPIC INVESTIGATION

The surface effect produced on galena, sphalerite, and pyrite by zinc sulfate and sodium cyanide was described in a recently published paper.³ The data given in the present article are the results of microscopic study of the surface effects produced on pyrite when exposed to contact with sodium cyanide and other reagents in a flotation cell, under conditions described in the preceding paragraphs.

³ E. L. Tucker: *Loc. cit.*

The method of procedure was the same as that previously employed and described as follows: "A piece of freshly broken sulfide mineral, about 5/16-in. long, that showed a clean, plane face was used for each test. One-half of the surface of the mineral to be examined was coated with melted paraffin to prevent solution contact." The mineral particle was attached to the impeller shaft of a small M-S type machine and agitated in a distilled water solution containing sodium cyanide and lime, respectively, and also in a solution containing both cyanide and lime. After 10 min. agitation the mineral particle was removed from the cell, washed with a jet of distilled water, the paraffin carefully removed, and both the protected and unprotected portions of the surface

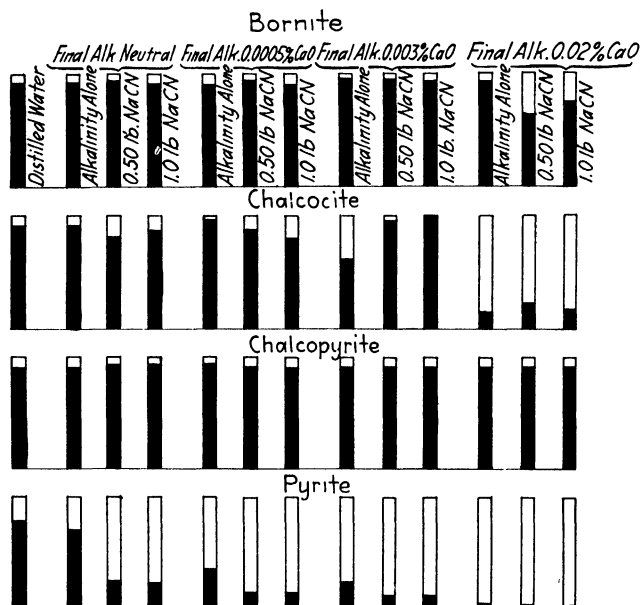


FIG. 1.—GRAPHIC PRESENTATION OF DATA OF THE EXPERIMENTAL WORK.

examined under the metallurgical microscope. As before, blank tests were run using distilled water alone, but no evidence of surface oxidation was observed.

The photomicrographs show both surfaces at the dividing line between the portion of the particle protected from solution contact and that which was exposed.

Fig. 2 shows that a distinct effect is produced on the surface of pyrite when sodium cyanide and lime are introduced into the flotation circuit. As shown in the photomicrograph, the effect cannot be described accurately as a film since the entire surface is not uniformly covered. This statement is true in regard to both photomicrographs, although each

shows the results produced under different conditions. Under the microscope the coating is resolved into innumerable individual particles, distributed over the exposed surface in a fairly uniform manner.

It is noticeable that the adsorbed particles vary considerably in size especially when both lime and cyanide were used. Comparison of the lime-cyanide coating with that produced by cyanide and lime, respectively, as shown in Figs. 3, 4, suggests that the larger individuals in Fig. 2

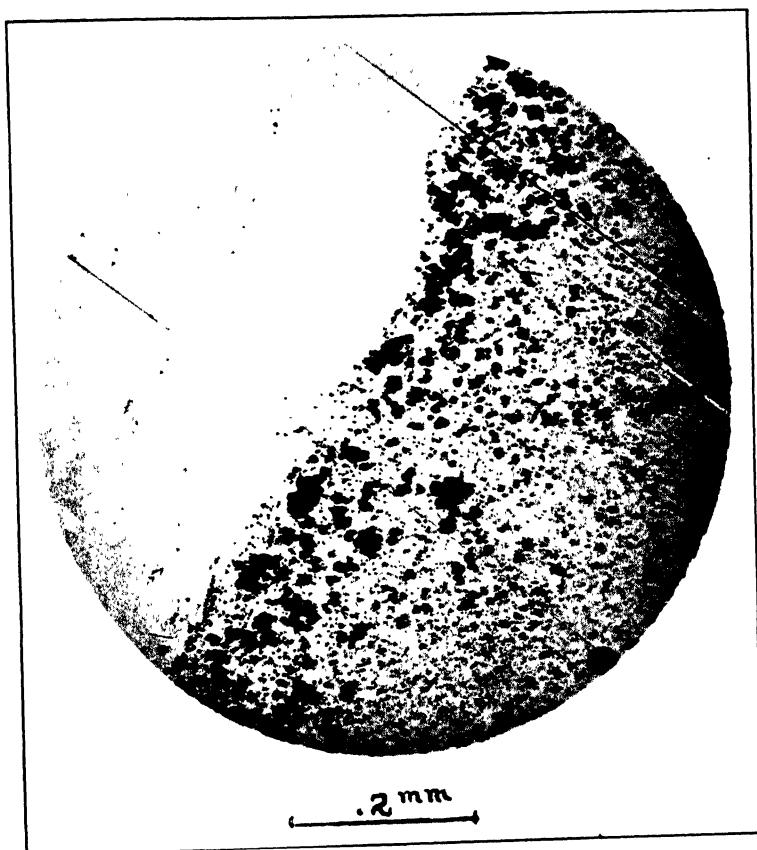


FIG. 2.—UNRETOUCHED PHOTOMICROGRAPH SHOWING THE SURFACE EFFECT PRODUCED ON PYRITE BY COMBINED CYANIDE AND LIME. $\times 125$.

may be attributed to the lime, which seemingly builds up, forming agglomerations composed of a number of small particles. In Fig. 4, which shows the deposit resulting from the use of lime alone, the particles are larger than those resulting from the use of cyanide alone as shown in Fig. 3. The deposit resulting from the use of cyanide alone consists of particles of considerably smaller average size than those produced by combined lime and cyanide or by lime alone. Their distribution is also more uniform and they apparently adhere more tenaciously to the surface

of the pyrite than is the case with lime alone. In the case of lime and cyanide together it may be that the smaller particles of salts due to the effect of cyanide serve as a nucleus around which the lime particles build up; this may also account for the more permanent depressing effect on the pyrite than when lime alone was used.

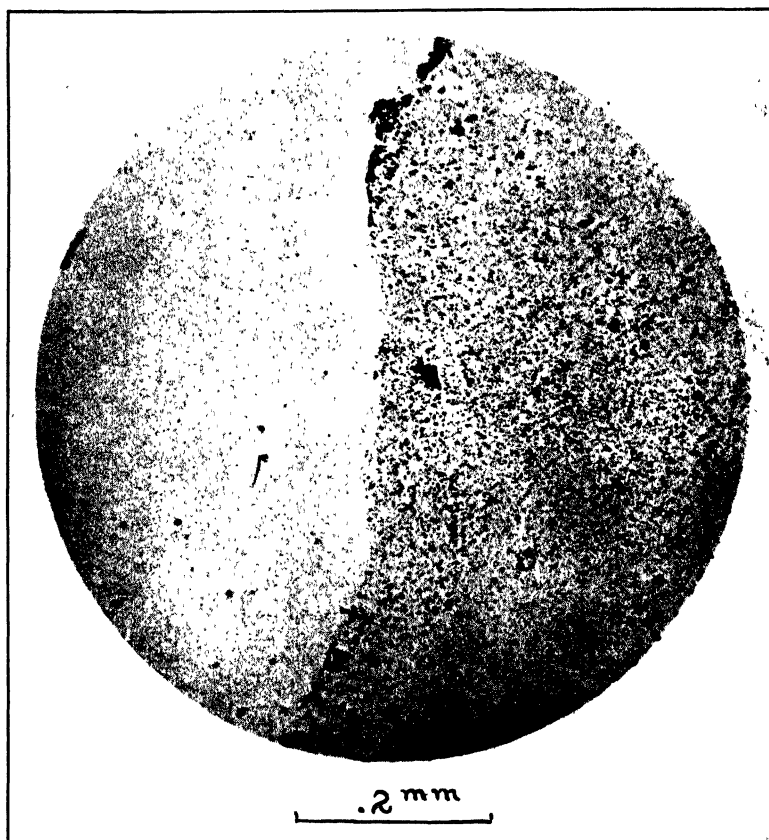


FIG. 3.—UNRETOUCHED PHOTOMICROGRAPH SHOWING THE SURFACE EFFECT PRODUCED ON PYRITE BY CYANIDE ALONE. $\times 125$.

Although these photomicrographs were taken through the medium of the metallographic microscope, the surface deposits are clearly visible under the ordinary binocular microscope. With the aid of this instrument the absorbed salts are distinctly visible and are commonly white in color, although in some instances the pyrite surfaces presented a somewhat bluish or tarnished appearance similar to that produced by incipient surface oxidation.

The surfaces shown in the photomicrographs are crystal planes and were selected for photographic reasons. The microscopic examination,

however, was not confined to these portions and the surface effect was found to be the same on all surfaces that had been exposed to solution contact. The study of the effects resulting from the procedure outlined was further extended to include an examination of the pyrite particles composing a regular test charge treated in the cell under the same solution conditions as obtained when the larger crystal faces were prepared for study.

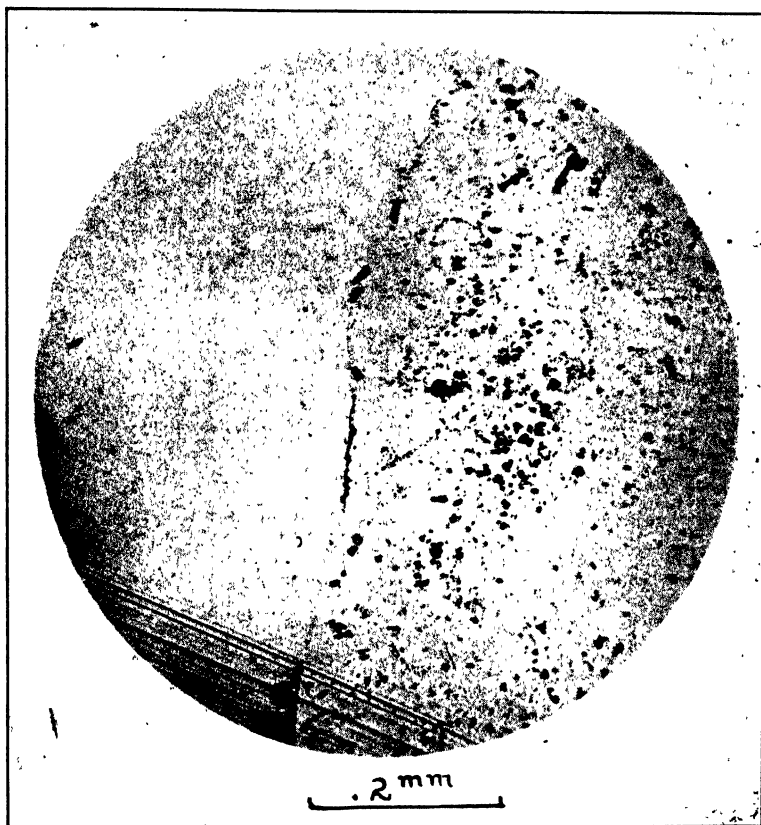


FIG. 4.—UNRETOUCHED PHOTOMICROGRAPH SHOWING THE SURFACE EFFECT PRODUCED ON PYRITE BY LIME ALONE. $\times 125$.

The surface of the small pyrite particles composing the charge showed the adhering salts similar to those obtained on the large test pieces, thus indicating that the abrasion due to collision of the mineral particles during agitation in the cell has no apparent effect on the formation of the deposit described.

Qualitative microchemical tests made on salts removed from the surface of the pyrite crystal that had been exposed to contact with the lime-cyanide solution gave definite reactions for iron and lime. A similar

test made on the salts resulting from contact with cyanide alone gave with KSCN the characteristic claret red coloration indicative of ferric iron.

SUMMARY

1. The laboratory experimental work has established a table of normal relative floatability for chalcopyrite, chalcocite, bornite, and pyrite in water under standard conditions.

2. The use of cyanide and lime separately and in combination with each other was investigated and the effects produced on the floatability of the several minerals shown graphically.

3. The evidence based on the experimental data indicates that the use of cyanide in conjunction with lime produces a more depressing action on pyrite than lime alone.

4. Comparison of the surface effects produced by lime, and lime and cyanide in conjunction, apparently bears out the results obtained experimentally, that is, that the lime-cyanide combination is a more active retarder of pyrite floatability than lime used independently.

5. Microscopic examination of pyrite surfaces that have been subjected to solution contact shows definite surface effects in the form of adsorbed salts.

6. Marked action of high lime alkalinity in depressing the floatability of chalcocite is shown and the necessity for alkalinity control within restricted limits is suggested when elimination of pyrite from chalcocite ores is contemplated.

7. The surface effect produced on pyrite when exposed to solutions in the flotation cell containing lime and cyanide, or either salt alone, is not a film but consists of particles either alone or agglomerated, which adhere to the surface.

8. Microchemical tests made on particles removed from the surface of treated pyrite show the presence of ferric iron when lime and cyanide were used and also when cyanide was used without lime.

Further investigations of the action of sodium cyanide on pyrite and its role in the selective recovery of the copper sulfides from ores containing pyrite are being conducted, but from the evidence available it would appear that a feasible method for the elimination of pyrite during copper concentration is indicated by the work described.

Mining and Preparation of Eastern Molding Sands

BY R. M. BIRD,* PHILADELPHIA, PA.

(New York, Meeting, February, 1926)

FEW persons outside of the foundry trade have any conception of the great variety of sands now regularly specified and furnished, nor of the differences in foundry practice frequently resulting from apparently minor changes in sands. Conditions in each locality where the sands are mined and prepared necessitate special equipment designed to perform the work efficiently. The description that follows of the foundry-sand producing operations is typical of the areas in New York and New Jersey, and particularly refers to the operations of the George F. Pettinos Co.

A few years ago the so-called Albany sands were dug by simple methods and hauled by horsecart to railroad. Depletion of sand near railroad sidings and extended use of automotive power have appreciably extended the area from which sand is now being dug. It is not unusual to haul 5 miles to the railroad.

As stripping is quite shallow, 6 to 18 in., and the banks of usable sand generally run from 12 in. to 4 ft., it is economical to work the bank by benches so narrow that the overburden can be thrown by hand shovel to the exposed bottoms. In effect the top soil goes back to where it was, but on a lower level. Consequently the general surface appearance of a mined acreage is the same as before. This condition is in fact customarily required when a farm owner sells his sand in the ground. After such replacement, in the course of 3 to 5 years the soil is no less fertile than it was before mining.

The sand itself varies as to grain and bond vertically and also along the breast. No mechanical equipment has been developed to compete with hand shovels and no machine has as yet been devised that grades the sand as required. Uniformity of sand, as shipped, depends first, last and all the time on the man on the job. Mixing equipment can change the appearance of the sand and mask its lack of uniformity, but it will never correct wrongly graded sand, dug from the bank. Modern methods of testing are helpful in setting up standards against which the man in the bank can compare his sands, but a good bank foreman is the only assurance that the sand, as dug, matches the required sample.

* George F. Pettinos Co.

Thus Albany sands of variable quality are hand dug from shallow banks and delivered direct to wagons or trucks from which they are in turn shoveled direct into the railroad car, or piled. Their "preparation" is only the handling they receive from the bank to the foundry floor.

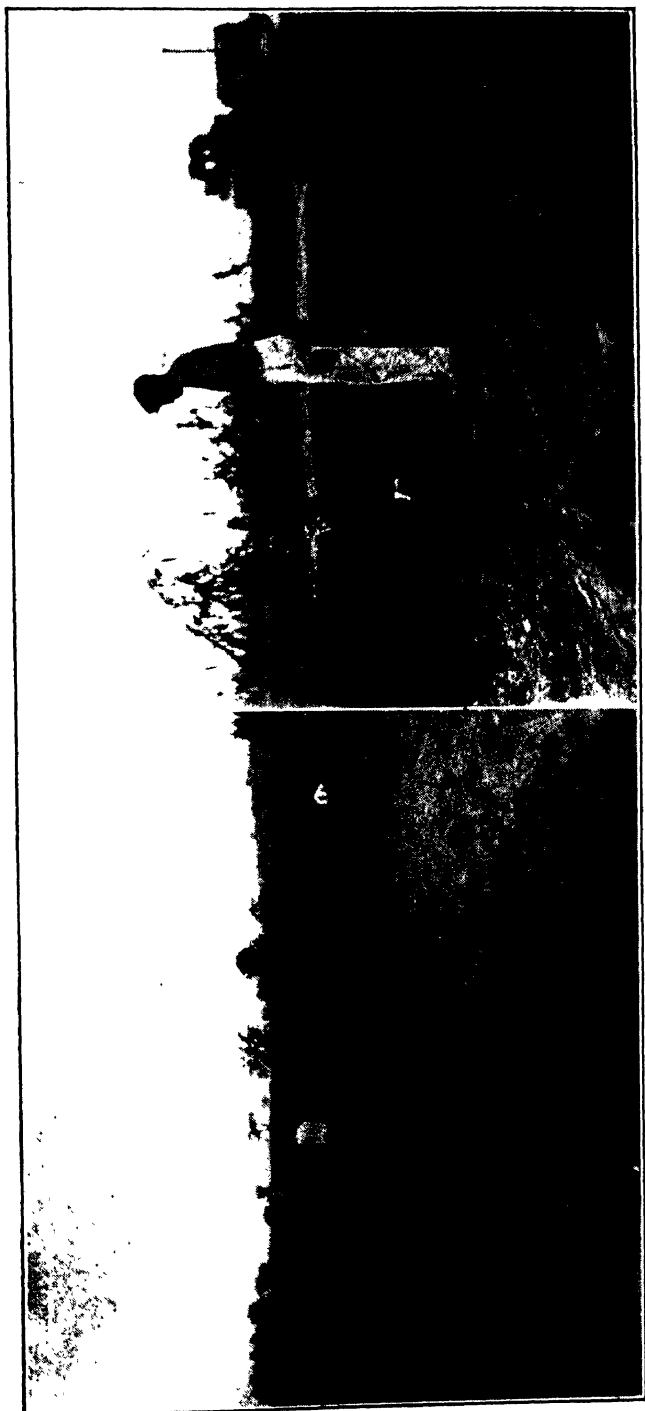
These sands are, normally, easy to dig as they are relatively free from stones. But when the winter frost of that very cold district gets into the bank, digging is difficult and selection practically impossible. Furthermore, frozen sands whether or not thawed out before unloading from a box car are not pleasing to the eyes of the foundry superintendent. In April, May and June when the frost is finally all out of the ground, operations are bad. The wet sand is difficult to select and the muddy fields and roads slow up and increase the difficulties of transportation. Digging of the bank from the time frost hits it until dried out after the thaw is to be avoided as far as practicable.

In anticipation of the emergency foundry requirements during that period it is good practice to dig and pile sand by grades during the season of good weather. For operating convenience some producers pile extensively, which allows more latitude to their operating men.

Lumberton sands, of the Mt. Holly, N. J., district, present the same handling problems as do the Albany sands. The stripping runs from 12 in. to $3\frac{1}{2}$ ft., and the sand from 18 in. to 5 ft., averaging about 3 ft. in the bank. The sand is more regular as to quality than the Albany sands. Devastations by the Japanese beetle have resulted in severe restrictions by the Department of Agriculture, culminating in the period from July 15 to Sept. 1, when the only shipments allowed outside of the quarantined district are in box cars fumigated by carbon bisulfide.

South Jersey sands, notably those from the Millville district, present totally different problems to the producer. Here the coastal plain deposits yield sands of variable quality. On one 1750-acre property is found the widest range of quality imaginable, from the coarsest gravel to 100 average mesh. Probably no one factor has been more prominent in making Millville sands stand out as they do than the fireclay which is dispersed through the various deposits in percentages running up to 30.

Stripping is naturally the first operative problem (Figs. 1 and 1a). The overburden to be removed is seldom less than 3 ft., running to about 6 ft., with $5\frac{1}{2}$ as a fair average. The country is rolling and fairly hilly, and it is difficult to lay out railroad tracks and keep under a maximum gradient of 5 to 100 ft. The land is overgrown with fairly dense bush and trees up to 6 in. in diameter. It used to be the tradition that the only possible way of removing this material was by horse and cart, but in 1924 trucks were tried out for this work. Loading of overburden by gasoline power shovel to 1-ton trucks has proved very satisfactory, although the wear and tear on truck engines is excessive, and cutting of pneumatic tires by stumps is, to some degree, unavoidable.



FIGS. 1 AND 1a.—STRIPPING SANDS AT ALBANY, N. Y. (LEFT); AT MT. HOLLY, N. J. (RIGHT).

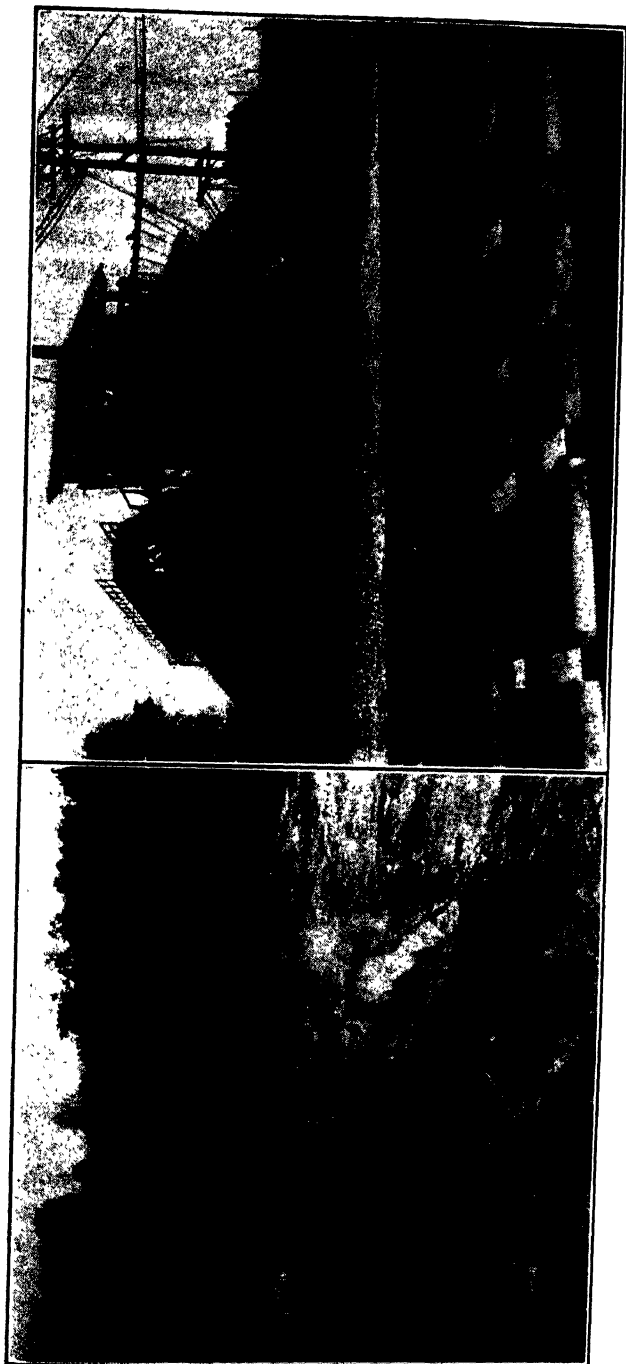
The Millville stripping operation is planned on the basis of as many trucks as can be effectively operated, having in mind the restrictions of space and the distance of hauling. Generally, one gasoline caterpillar shovel, with a 1-yd. bucket, one dip to the truck, should keep four trucks going an average distance of 75 yd. to the dump, 175 trips each in a 9-hr. day. There are, however, many restricted operations where the stripping cost is excessive.

To dig sands 5 to 30 ft. high in the bank economically requires mechanical equipment. Old steam traction shovels, with $\frac{5}{8}$ - and $\frac{3}{4}$ -yd. buckets, are being replaced by gasoline caterpillar shovels with 1-yd. buckets. The flexibility of the caterpillar offers such an extension in the scope of operation that it is conservative to figure that it does the work of two of the older type of shovels. However, the decision to replace steam by gasoline in a distinctly steam-operated district and with a steam trained organization was reached only after a thorough study. The results have been gratifying. One unlicensed operator replaces a licensed engineer and fireman. At Millville the cost, delivered at the shovel, for gasoline is 24 per cent. over the cost of coal at Millville, but time to fire up is eliminated, and there is no water to haul a half mile or more to the remote bank or stripping operation.

Over 1924 and 1925 the direct operative cost, including repairs, at the Pettinos plant is figured as \$20 per day for the gasoline shovel and \$25.70 for the steam machine. The chief source of trouble and expense with the gasoline shovels lies in the repair item of \$10.30 per average operating day. At least three-quarters of this represents replacements of caterpillar drive and treads. The gasoline shovels move around considerably more than the steam, and the movement of this heavy equipment over soft sand constitutes severe duty upon wearing and bearing parts. Still, the gasoline shovel manufacturer can do much to improve his designs and materials. In this connection experience justifies our belief that properly designed oiled bronze or babbitt bearings are superior to manganese steel for wearing parts, such as treads, sprockets, shovel teeth and centrifugal pump members, where, as locally applied, they are subject primarily to abrasion and not to shock.

At the Pettinos plant most of the Millville banks are dug with power shovels and loaded on 1-ton trucks or 4-yd. dump cars, running on three 3-ft. gage track, 30-lb. rails, hauled by 11- and 14-ton steam locomotives (Fig. 2). Hand digging is resorted to where shallowness or inaccessibility of banks prohibits the use of a power shovel, or when more intimate turn-over of the sand is desired for direct rail shipment.

River bottom sand, for the open-hearth and steel foundry, is dug under water by a stiff-leg derrick with $1\frac{1}{4}$ -yd. orange-peel bucket, and piled on the bank for subsequent loading into cars or trucks by power shovel as desired. The sands from the various pits may go direct to the railroad by truck or to the mixing, screening and storage plant by truck



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or car, or direct to boat by car. The prepared material on stock is delivered to railroad or boat by truck.

Single purpose screening or blending of two definite sands is fairly easy to accomplish. Revolving screens to eliminate stones from foundry gravels are numerous in southern New Jersey.

Equipment for handling large tonnages of sharp sand presents no difficulties not readily solvable, and the same is true to a lesser degree for heavily bonded sands. But these problems are totally different, and the equipment satisfactory for one will not do for the other. Gravity



FIG. 3.—MINING SANDS BY HYDRAULIC METHODS, NEW JERSEY.

is a servant for sharp sand, but heavily bonded sand, when moist, as it is the year around in the ground, requires other treatment. Sharp sands are readily screened, but bonded sands screen with great difficulty when damp. Sharp, fine sand gets into bearings and mixes with the lubricating oil with much the same results as would be expected of carborundum as a lubricant.

The method of work adopted must meet all of these conditions. It is necessary to deliver sand from all pits to a common point, then to mix and screen in any combination, and finally to deliver to stock any prepared material at a rate equal to the capacity of the digging and

transportation equipment. Since April, 1925, we have been operating at Millville the plant (Fig. 2a) which represents our attempt at a solution. It comprises several unusual features.

Three parallel railroad tracks rest on the tops of the side walls of two concrete trenches, 65 ft. long, 5 ft. wide at the bottom, and of 5-ft. average depth. Dump cars on the center track can dump into either trench. From each outside track they can dump into the adjacent trench. Thus the trains can deliver into either trench layers of any combination of material desired. This is the first step in the control of any definite mix. In each trench a $\frac{3}{4}$ -yd. bottomless scraper drags the material to either one of two conveyor belts passing crosswise underneath both trenches. One of these, 24 in. wide, runs up to an elevation of 36 ft. above the ground, and thence horizontally 180 ft., at any point of which a tripper will throw off the sand. The second belt, 30 in. wide, carries the sand up to a revolving screen through the mesh of which it drops on to the first belt. The oversize from this screen is passed through a beater to break up any clay lumps and bonded aggregates which it then delivers to a second screen. The material passing through this screen also falls on to the first belt. The waste material, consisting almost entirely of stones, becomes an occasionally salable by-product.

The flexibility of this equipment is at once apparent. Two materials, both of which require screening, such as heavily bonded gravel and coarse grit, go into a common trench and through the screen out to stock. A fine sand, not requiring screening, such as river bottoms, fed through one trench to the belt going direct to stock, meets a coarser, slightly bonded sand, fed through another trench and the screen plant, when the latter sand drops on to the first belt.

The scraper operators are responsible for the delivery to the respective belts of the sands in proper proportion. Whatever lack of uniformity in feed exists disappears in the stock piles, which for standard mixes are cones of 2500 tons built up layer by layer and then dug by power shovels up the full height maintained in the pile.

One gasoline shovel and four trucks will load a 900-ton boat in a 9-hr. day. A 325-hp. Diesel engine tug tows two 900-ton boats for coastwise deliveries, so providing for waterway transportation.

At this point let me comment on one of the many inconsistencies which are frequently met, in comparing methods in two fields. In the Albany district our men condemn the popular 1-ton dump truck so extensively and successfully used throughout New Jersey; but a heavy truck from Schenectady finds a similar lack of favor at the Millville operations.

Finally, hydraulic mining (Fig. 3) is not unusual for core sands. Such operations are substantially alike. The overburden, averaging 5 ft. at one operation, and running from 8 to 20 ft. at another, is removed

by power shovel and trucks. Centrifugal pumps, from 4 to 12 in., are mounted on scows, driven by electric motors, and suck the sand and water through spiral-riveted pipes to the permanent washing plant up to 2000 ft. away. The sand pumped does not exceed 15 per cent. of the total weight of sand and water. The washing is done generally in a reel for removing stones and coarser sands. The remaining preparation consists merely in the washing out of the clay from the sand by means of a series of wooden wash boxes from each of which the sand is removed by screw conveyor or scraper. This type of operation is popular where the bottom of the bank of usable sand is far enough below water level to permit the floating of a scow. The equipment is simple and the operation economical.

DISCUSSION

W. M. WEIGEL, Washington, D. C.—How do you differentiate between sharp and strong sands?

R. M. BIRD.—Sharp sand is a silica sand containing little bond. How much bond is necessary to put it out of the so-called sharp class is a matter of personal opinion and tradition. Some call a silica sand containing 3 per cent. clay a strong sand, particularly when it goes into the furnace bottom. Others, in steel foundry work and particularly in certain iron foundries of Philadelphia, classify a sand containing 6 per cent. clay as sharp. It is a variable matter, but, generally speaking, I would say a sharp sand has no strength when bonded up, that is, when taken in the hand and molded out, whereas a strong sand has appreciable strength in the hand.

W. A. NELSON, University, Va.—Is bentonite being used anywhere?

R. M. BIRD.—I know of no practical application of bentonite. It has been used experimentally by people like ourselves who are always looking for additional colloidal bonds and bonding clays, but, unfortunately, in the molding-sand industry of the East, you are limited by the ultimate cost per ton of the products as made against what you can get for it, and bentonite is out of the realm of practical application.

W. A. NELSON.—A New York broker said he was shipping the material to molding-sands' producers to mix with the molding sands. Do I understand that if you could get it cheaply enough, you could use it?

R. M. BIRD.—Yes.

W. A. NELSON.—It has the quality you need?

R. M. BIRD.—Bentonite is excellent.

W. A. NELSON.—What percentage would you want to use?

R. M. BIRD.—That is an open question, Mr. Nelson. I do not know that I am capable of answering it. Obviously the bentonite would

be shipped raw in order to conserve the freight rate to the point of its application, and then the question of how much bentonite you would use to bond up a ton of sand would depend entirely on the purpose of that sand.

W. A. NELSON.—Probably. What I wish to get at is this: How much demand would there be for bentonite, say annually, to start with, if it could be obtained at a satisfactory price?

R. A. BULL, Chicago, Ill.—I know of a steel foundry that has been experimenting with bentonite as a substitute for clay for steel molding sand, with very desirable results, although the bentonite costs about \$42.50 per ton delivered. It is sold under a commercial name, but it is actually bentonite from Wyoming.

W. A. NELSON.—There are deposits of that same material in the southern states. It is not quite so good, and it occurs in 5 or 10-ft. layers.

E. L. JONES.—A foundry in Milwaukee has been using bentonite for 2 or 3 years; about 3 per cent. is used.

H. RIES, Ithaca, N. Y.—Is the term "sharp sand" altogether a correct one, Mr. Bird? The grains of any of these sharp sands, so-called, are very distinctly rounded, not angular at all. And where do you draw the dividing line between the sharp sand and another one in the other class?

We have had some sands come to our notice that appear to be clean sands, apparently low in clay substance, and yet the A.F.A. fineness test showed that they contained as much as 10 and 12 per cent. clay substance and the bonding strength was quite low. Evidently the clay substance contained a minimum quantity of true clay.

I would also like to ask Mr. Bird or Major Bull about the refractoriness of bentonite.

R. A. BULL.—We have not made any tests to determine that, but the amount of bentonite used in what we call a facing mixture, the greater proportion of which is pure silica sand, is so small that apparently it does not noticeably affect the refractory quality of the mass.

The foundry I spoke of has used this material quite successfully to emulsify oil for making cores so that they get substantially the same result in bonding the core sands with about half the amount of linseed oil.

I am glad the discussion came up because if this particular foundry can secure the same or similar material at a substantial saving in price from \$42.50, they would be decidedly interested in that.

H. RIES.—Mr. Nelson, at what cost could bentonite be put on the market?

W. A. NELSON.—It would depend on the tonnage. If you could get a steady tonnage, starting with about a carload a day, so that you could

give steady employment—I suppose it would have to be underground mining—the cost would be something like \$10 a ton, with a freight rate of \$10 to the farthest point in the East. That would be from Kentucky. It might be less than that, because the freight rate on barite from Georgia to New Jersey points several years ago was about \$5 a ton. The fact that you would have to mine most of it underground eventually would run the cost up. It is in about 5-ft. layers in Kentucky. I think the Virginia material is a little too coarse. I may find some other layers more colloidal, but the Virginia material I have seen is standing on end and has been subjected to a good deal of pressure and has lost much of its elasticity. I do not believe it would be very good for your use, but the Kentucky product probably would.

As to the fusability, all of the analyses of bentonite I can remember showed a combination of sodium and potassium totaling from 4 to 6 per cent.

H. RIES.—Offhand I do not see any special reason why synthetic mixtures should not be used. I do not think that many synthetic mixtures have been used in the case of ordinary iron molding sands. Am I right on that, Major Bull?

R. A. BULL, Chicago, Ill.—Yes.

H. RIES.—It is rather easy to get iron molding sands of the proper quality, but if you desire to use the furnace bottom sand with clay added I should think it would work.

R. D. CARVER.—With the Albany sand about 20 per cent. goes through 270 mesh and considerable remains on the 200 and 140 mesh, the largest percentage being on the 270 mesh. With the furnace bottom sand, only 1 per cent. goes through the 270 mesh and there is about 36 per cent. on 100 mesh. That shows that the furnace bottom sand is more uniform, and with a small amount of clay added good results should be obtained. The clay substance washed out was 9.2 per cent. on the Albany sand and about 12 per cent. on the furnace bottom sand. That is why it was rejected. I think that the more uniform the sand the better it will be. Whereas it was brought out that the Albany sands are only 13 in. thick, these sharp sands, if I am right, can be dug in large pits and thereby make quite a saving in mining.

R. A. BULL.—The answer to this question depends on the variance with which the mixing is done in preparing the synthetic mixtures. If you have mechanical means for getting a good distribution of the materials, I should think the sands would work all right. Do you not think so, Mr. Bird?

R. M. BIRD, Philadelphia, Pa.—I think so.

R. A. BULL.—You would have to determine whether the cost of the preparation of the mix was such as to justify the use of it as against the cost of the sand mixed by nature.

R. M. BIRD.—I can answer on this point. I showed you a picture of bank sand about 5 ft. high which is shipped to the steel foundries and used almost entirely by the Chester Steel Foundries. It also goes to certain iron foundries. The clay runs 18 per cent. Below that there is the same general structure of sand, but due to varying water levels in past ages the clays have been washed out, so that operating with a stiff-legged derrick from the top about 4 ft. above the present high tide down to 10 ft. under water, where the clay has been practically all washed out, we get an average in that pile of about 6 per cent. clay. That is furnace bottom sand. In other words, the furnace bottom sand you are discussing is simply steel molding sand with the clay washed out. The clay can be put back again, as Major Bull says, if it is properly mixed in.

W. M. WEIGEL.—We cannot look at this matter in the same way for iron molding as in the case of synthetically-bonded sands for steel molding. Most of the iron sand contains a considerable amount of bond, not clay, but hydrated iron or something like that with a considerably different bonding quality from that of the ordinary clay that may be used for steel molding sand. That point might be important in the preparation of a synthetic sand.

C. A. HANSEN, Schenectady, N. Y. (written discussion).—Bentonite from Belle Fourché (South Dakota) has been tested to some extent as a bonding material for molding sands. The bentonite was finely ground and mulled with a clay-free silica sand, the mixture being tempered to molding consistency in the mill. More than 20 well known and commercially important domestic and foreign plastic refractory clays have been tested to date in the same manner.

Finely-ground bentonite becomes gelatinous almost immediately upon the addition of water; all of the clays require considerable time to slake, from several minutes to approximately an hour. This is reflected in the ageing of the freshly mixed sand, the clays requiring from several minutes to approximately an hour to develop maximum strength. Weight for weight, this bentonite was somewhat more than twice as effective as the best clay in developing green strength in a molding sand.

Cores, made from bentonite and sand and baked at low temperatures (under 150° C.) developed much greater dry strengths (tension and compression) than the best clay-sand mixtures.

So much for the advantages, for they were outweighed by disadvantages. This bentonite dehydrates very readily and, when once dehydrated, its bonding value seems to permanently disappear; it has no appreciable life in the molding sand heap. Its fusion temperature is very

low; Seger cones made with equal weights of bentonite and sand fused to a thin puddle at 1200°C ., both in an oxidizing atmosphere and in hydrogen. The actual fusion point was not determined, but it is evidently much below 1200°C .

Bentonite, however, is not a specific material of fixed chemical composition. I understand that bentonites range from 3 per cent. to 12 per cent., approximately, in alkali metal content. It would not, therefore, be fair to generalize too far on the strength of the results obtained with one bentonite variety, although I believe that the variety actually used is one of the few commercially important varieties.

The Use of Standard Tests of Molding Sands

By H. RIES,* ITHACA, N. Y.

(New York Meeting, February, 1926)

IN THE marketing of mineral products, it is always highly desirable for both the producer and the consumer to be able to discuss things in a common language, and this can only be done if there are standard methods for expressing the properties of the raw materials. Having developed such a form of expression, the next step would be the making of specifications, which may serve as a basis for selecting raw materials.

Considering the large number of non-metallic minerals that are used, there are not a few for which there are no standard laboratory tests to be used in determining their properties, or even standard specifications on which grades or market price may be based. Indeed in many cases the consumer simply requests the producer to submit samples, and rejects or accepts them without any explanation. Could the producer know in advance just what the consumer needed, time and money might often be saved. It appears to the writer that it is of the highest importance to devise standard laboratory tests wherever possible, as this enables the consumer to state definitely what he needs, and is of great assistance to the producer. It should also work to reduce misunderstandings and disputes.

In the case of sands, we find that they show a wide variation in their character, ranging from those that are so coarse as to be of gravelly nature to those that are so fine that they might be classed as silt; and from very clayey ones to those that are practically free from clay. For this wide range of sands, we have a corresponding variety of uses, which are based mainly on the physical properties of the sand, although these are not always very definitely stated. The chemical composition need rarely be considered, if the sand is of siliceous nature.

To determine and express these properties there should be standard tests, which are to be followed in all cases where the material is tested in the laboratory.

The use of sands for foundry work (making molds or cores) is old, and it has been recognized for some time that the important properties to be

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considered include bonding strength, permeability, texture, refractoriness, and life. We have, however, lacked uniform methods for measuring and expressing these properties. In many cases, the first two have been referred to as high or low, or the texture may have been described as fine, medium, or coarse. It is true that a number of tests for determining the properties of foundry sands have been described and used by different persons in both Europe and America, but as a rule the results have not been comparable, because the tests were not made under uniform conditions. That the results were not comparable was overlooked by many, until the problem had been carefully studied.

Within the past three years, the Joint Molding Sand Research Committee organized by the American Foundrymen's Association and the Engineering Division of the National Research Council, through its Sub-Committee on Tests, has devoted considerable time to this problem, and, with financial assistance from the former organization, has supported much necessary research with the object of obtaining reliable data on which the formulation of standard methods of testing could be based. The tests recommended together with the method of making them have been described elsewhere;¹ they include tests for measuring the fineness, permeability, bond, and dye absorption. There still remain to be developed standard methods for determining, among other properties, the refractoriness and life of the sand, for expressing the grade or texture, by a single figure if possible, for testing the properties of core sands or core mixtures, etc. Much progress has been made toward formulating these.

Of prime importance however is the proper use of the data obtained through the medium of standard methods of testing, and I wish to stress this point particularly because there exists some misconception on the part of not a few.

The writer has frequently been asked to state what permeability, bond strength, etc., a sand should show if it is to be used for casting iron, brass, or some other metal. This question cannot be answered definitely for several simple reasons. Sands showing a fairly wide range of certain properties at least can be used for casting any one of these metals, and the type of sand used is governed in part by the fact that the size alone of the casting will affect the type of sand to be employed, or artificial causes, such as the method of venting the mold, may exert a controlling influence.

It is possible, and quite probable, that some day we shall be able to state, for example, that a sand to be used for brass castings up to, say, a certain size, should show a certain range of permeability, bond strength, and fineness, but we cannot do this until we have more data. But though the accomplishment of this may be delayed, it does not in any

¹ *Trans. Amer. Found. Assn.* **32**, Pt. 2

way detract from the value of the standard tests. On the contrary, their widespread acceptance and employment has demonstrated their usefulness in other directions. They can and should be used both as a check and as a form of specification, although this last word may not be altogether satisfactory to some.

There is apparently no valid reason why the consumer should not demand a sand showing a certain range of permeability, bonding strength, dye absorption, and texture. It seems reasonable to assume that the producer can meet this demand by mining a sand of uniform quality; or, by mixing two sands, produce a blend of the requisite qualities. Some foundries even now are purchasing sands on this basis, and in the writer's opinion this practice will spread. It represents a form of specification.

The other use of standard tests will be in the foundry,² where the foundryman finds that the best results are often obtained by keeping the properties of his heap sand close to certain values of moisture, permeability and bonding strength. These values may be originally obtained by using a single sand or a mixture of sands, and daily checks of the sand heap are made to determine how close it is running to requirements. If there is a deviation, the necessary correction can be made by the addition of some new sand or by regulating the moisture content, if that is necessary, because it is known that both permeability and bond strength vary with it. We thus have a form of specification that the foundry worker must meet. Testimony by foundrymen now using these standard control tests in their daily work shows that many dollars are saved, by reducing defects caused by the sand being in a bad condition.

The value of the use of such standard tests is, furthermore, brought out by the fact that there are over 100 standard permeability apparatus in use, and their employment is spreading. They are employed by both producers and consumers.

Much confusion still exists as to the grading of sands. The term grade refers solely to the texture of the material and at present there is no uniformity in expressing it. Some producers grade their sand according to numbers, others according to letters, each adopting his own series. Even in the same district, the same numbers may not represent the same grade when used by different producers; such a situation calls for a speedy remedy. There is absolutely no good reason, why six sands of the same grade, produced by as many firms in separated parts of the country, should not be known by the same number or letter. Such uniform grading is of particular value to the foundryman who may desire to obtain sand from a source not hitherto drawn on. Fortunately, a sub-committee of the American Foundrymen's Association is now work-

²H. W. Dietert, Commercial Application of Molding Sand Testing. Amer. Found. Assn. preprint 425 (1924). F. S. Wolf, and A. A. Grubb: Molding Sand Reclamation and Control Experiments. Ibid, preprint 430 (1924).

ing on this problem, having as a basis for study the fineness tests of several hundred sands that have been collected in many different areas of the United States, by the various state geological surveys cooperating with the American Foundrymen's Association.

DISCUSSION

W. M. WEIGEL, Washington, D. C.—Professor Ries, would you care to anticipate how much consideration is being given the refractoriness of molding sands—is that still under investigation?

H. RIES.—The refractoriness and life of a molding sand are both important properties. We naturally do not want to use a sand that is going to fuse very rapidly at the temperature at which the metal can be cast or one whose bond will be easily destroyed. We have not yet recommended a standard test for determining the refractoriness of molding sands. That question is under investigation. The Bureau of Mines Station at Columbus and the Canadian Bureau of Mines are cooperating with us on the problem. We are hoping to get the reports from these institutions very shortly. Until then we cannot proceed with the formulation of a standard test for refractoriness and life.

R. D. CARVER, Everett, Mass.—I have run some tests on an Albany No. 2 sand used in an iron foundry making castings from 1 to 25 lb., and a furnace bottom sand and obtained certain properties. This furnace bottom sand has been rejected as having too high a clay content for the open hearth. I want to use this as a molding sand by adding 1 or 2 per cent. of clay. I am of the opinion that this furnace bottom sand can be used even better than the Albany sand for molding sand.

At 3.8 per cent. moisture in the furnace bottom sand I get a maximum strength of 155 gm. This is more than that obtained with the No. 2 Albany sand which gives a maximum strength of 135 at 4.8 per cent. moisture. The strength of the furnace bottom sand is too low at the moisture content at which we wish to use it and therefore we propose to mix with it a clay bond. We get the best results in the foundry when the moisture content of the sand is between 5 and 6 per cent. The maximum permeability in the furnace bottom sand is 145 at 4.4 per cent. moisture and in the No. 2 Albany, only 53 at 7 per cent. moisture. I note from Mr. Bird's paper that Albany deposits average about 18 in. in thickness and vary considerably in properties; whereas, the sharp sands in New Jersey occur in large banks. Can we not get more uniform results by using this sharp sand and adding the correct amount of bond?

American Glass Sands, Their Properties and Preparation

BY CHARLES R. FETTKE,* PH. D., PITTSBURGH, PA.

(New York Meeting, February, 1926)

IN THE present day manufacture of glass nearly pure quartz sands are used almost exclusively as the source of the silica, which is the major constituent of all common varieties of glass. Ordinary soda-lime, such as bottle, common tableware, plate, and window glasses, contains from 65 to 75 per cent. of silica.

OCCURRENCE

Glass sands occur in nature either in the form of loose, unconsolidated sediments or in deposits in which the individual grains have been more or less thoroughly bound together by some cementing agent so as to form sandstones. While deposits of sand and sandstones occur both widely and abundantly distributed, deposits that are sufficiently free from other constituents than quartz grains, so that they can be employed in the manufacture of the better grades of glass, are, comparatively speaking, of rare occurrence.

The major portion of the glass sand produced in the United States comes from sandstones. In order to be suitable for glass sand, they should be rather friable. The rock should break down readily along the cementing material between the grains and should not break across the grains rather than along the bond. Some of the sandstones used are so friable that only light shots of slow-burning dynamite are necessary to disintegrate them sufficiently for hydraulic mining, while others have to be passed through crushers in order to disintegrate the rock into its individual grains.

MINERALOGICAL COMPOSITION

An ideal glass sand is made up entirely of grains of the mineral quartz free from inclusions of foreign substances. Sands containing 100 per cent. silica, however, are not found in nature, although some very nearly approach this composition.

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Minute inclusions of foreign substances are sometimes present in the quartz grains themselves. These may be divided into gaseous, liquid and solid—the latter usually consisting of minerals of various kinds. The liquid in most cases is water, but liquid carbon dioxide may also occur. Gaseous bubbles often accompany the liquid. The milky-white color developed in certain quartzes is generally due to the reflection of light from inclusions of gas and liquid. Among the solid inclusions that may occur in quartz grains are a considerable number of minerals. One of the most common of these is rutile, which often occurs in quartz as extremely thin microscopic needles. Minute crystals of apatite and ilmenite abound in some quartz grains. Other minerals occasionally found as inclusions are needles of actinolite, chlorite, epidote, tremolite, and tourmaline. These are the most common mineral inclusions, but others have also been found in certain quartzes.

Besides the minerals that may occur as minute inclusions in the quartz grains themselves, there are a considerable number of others that may be present in very minor amounts in glass sands either as individual grains or as thin films upon the surface of the quartz grains. Among those that have been identified in various American and foreign glass sands are andalusite, apatite, calcite, chlorite, cyanite, dolomite, epidote, feldspars (including microcline, orthoclase and plagioclase), garnet, hematite, hornblende, ilmenite and its alteration product leucoxene, kaolinite, limonite, magnetite, micas (including biotite, muscovite, and sericite), rutile, staurolite, titanite, tourmaline, and zircon.

CHEMICAL COMPOSITION

When a complete chemical analysis of a glass sand is made there are almost invariably found to be present, in addition to the silica which constitutes the bulk of the sand, minute quantities of alumina, ferric and ferrous oxides, lime, magnesia, titanium oxide, traces of the alkalies, varying amounts of water, and occasionally a little organic matter in the form of coal or decayed vegetation. Some of these constituents are harmless, while others have a very deleterious effect upon the glass.

According to the committee on standards of the glass section of the American Ceramic Society, the chief criterion for a good glass sand is that it should be practically all silica and contain very little iron. The sand must not be contaminated with stripping dirt or contain any crushed stones or pebbles. These impurities are often insoluble in the melting glass, producing "stones." The committee working in cooperation with the U. S. Bureau of Standards has drawn up the following tentative specifications for silica sand for glass-making:¹

¹ Proposed Tentative Specifications for Silica Sand for Glass-making. *Bull. American Ceramic Soc.* (1923) 2, 182.

PERCENTAGE COMPOSITION OF SANDS OF VARIOUS QUALITIES

(Based on ignited samples)

Qualities	SiO ₂		Al ₂ O ₃		Fe ₂ O ₃		CaO + MgO	
	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.
First quality, optical glass.		99.8	0.1		0.02		0.1	
Second quality, flint glass, containers and tableware.		98.5	0.5		0.035		0.2	
Third quality, flint glass.		95.0	4.0		0.035		0.5	
Fourth quality, sheet glass, rolled and polished plate.		98.5	0.5		0.06		0.5	
Fifth quality, sheet glass, rolled and pol- ished plate.		95.0	4.0		0.06		0.5	
Sixth quality, green glass, containers and window glass.		98.0	0.5		0.3		0.5	
Seventh quality, green glass.		95.0	4.0		0.3		0.5	
Eighth quality, amber glass, containers. .		98.0	0.5		1.0		0.5	
Ninth quality, amber.		95.0	4.0		1.0		0.5	

In commenting on the above, the committee states that in view of the increasing use of alumina in a glass batch and of the varying amounts of iron allowable in green or amber glass, sand of lower grade may be used by many manufacturers. The above specifications show a variety of qualities and state more or less definitely the types of glass they may be used for. The quality number is not to be interpreted necessarily as an index to the value of the product.

Although glass sands may vary considerably in composition, depending on the type of glass that is to be made, it is highly desirable, and in most cases imperative, that there shall not be very much variation from shipment to shipment. The committee has proposed the following tolerances:

PERCENTAGE TOLERANCES IN COMPOSITION ALLOWED

(Based on ignited samples)

Quality	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO + MgO
1.	±0.1	±0.05	±0.005	±0.05
2.	±0.5	±0.1	±0.005	±0.05
3.	±1.0	±0.5	±0.005	±0.1
4.	±0.5	±0.1	±0.005	±0.1
5.	±1.0	±0.5	±0.005	±0.1
6.	±1.0	±0.5	±0.05	±0.1
7.	±1.0	±0.5	±0.05	±0.1
8.	±1.0	±0.5	±0.1	±0.1
9.	±1.0	±0.5	±0.1	±0.1

ALUMINA

Alumina is usually present in glass sands in the form of clay or kaolin-ite. It may, however, also occur as muscovite or sericite mica or feldspar. Clay or kaolinite, as well as the micas, can usually be largely eliminated by carefully washing the sand, but alumina present as feldspar cannot be gotten rid of in this manner. If the clay content of a sand is high, the iron content also is apt to be high as the clay is very likely to have limonite associated with it.

For first class optical glass the alumina content of the sand must be low, 0.1 per cent. or less, on account of its effect upon the optical constants of the glass. Plate glass manufacturers, as a rule, also prefer a low alumina content in their sands. Fulton² gives the desirable limit as 0.1 per cent. and the maximum permissible limit as 0.5 per cent. Shively,³ on the other hand, strongly recommends alumina to the manufacturers of glass containers.

The presence of small amounts of alumina in a glass sand is not necessarily detrimental in the manufacture of the ordinary types of glass. In some instances it is not only harmless but actually beneficial. At present, there is a tendency among many glass manufacturers to use more alumina in their glass than in the past.

Alumina decreases the solubility of glass in water, weak acids, and other reagents, which is very desirable in the case of bottles and chemical glassware. Baillie⁴ has shown experimentally that alumina has more influence in reducing the solubility of glass than lime. According to Shively⁵ the U. S. Bureau of Standards has checked Baillie's work and has obtained the same results, namely, that alumina substituted for lime in a glass batch will reduce the solubility of the resulting glass. Frink⁶ has also found that alumina decreases the solubility of glass in water, weak acids, and other reagents, but that in amounts up to 4 per cent. it does not offer as much resistance as does lime.

English and Turner⁷ have found that glasses containing considerable amounts of alumina have comparatively low coefficients of expansion. Their experiments have shown that alumina reduces the thermal expan-

² C. E. Fulton, Chief Ceramic Engineer, Pittsburgh Plate Glass Co. Private communication.

³ R. R. Shively: The Use of Alumina in Glass. *The Ceramist* (1924) May, 86.

⁴ W. L. Baillie: An Examination and Extension of Zulkowski's Theory of the Relation Between the Composition and Durability of Glasses. *Jnl. Soc. Glass Technology* (1922) **6**, 68.

⁵ R. R. Shively: The Use of Alumina in Glass. *The Ceramist* (1924) May, 83.

⁶ R. L. Frink: The Requirement of Glass for Bottling Purposes. *Trans. American Ceramic Soc.* (1913) **15**, 706.

⁷ S. English and W. E. S. Turner: The Thermal Expansion of Glasses Containing Alumina. *Jnl. Soc. Glass Technology* (1921) **5**, 183.

sion of trisilicate glasses, not only very much more than calcium, but very much more so than magnesium. Shively, likewise, has observed that by replacing part of the lime in glass batches with alumina, the resulting glass withstands much more rapid changes of temperature without breaking than the higher lime glasses.

An Aid in Preventing Devitrification

It is generally conceded by glass chemists that alumina aids in preventing devitrification. Dimbleby, Hodkin and Turner⁸ state that there is abundant proof of the value of alumina in preventing devitrification. Hovestadt⁹ attributed the ability of Thuringian thermometer glass to withstand repeated melting and working without change to the fact that the 3.66 per cent. of alumina present in the Martinsroda sand from which it was made tended to prevent incipient crystallization or devitrification.

The annealing temperature of alumina-containing glass is generally less than that of the corresponding lime glasses, according to English and Turner.¹⁰ No case was found in which it was greater. In other words, annealing is rendered easier by the presence of alumina.

It was for a long time believed that alumina tended to decrease the fusibility of glass. Singer,¹¹ however, has carried on some experiments on the influence of alumina on the fusibility of lime-soda glasses in which he found that, instead of decreasing, it increases the fusibility of this type of glass even in amounts up to 8 per cent. of the total composition of the glass.

Singer worked with glasses of the composition $.5\text{Na}_2\text{O} : .5\text{CaO} : 3\text{SiO}_2$ and $.4\text{Na}_2\text{O} : .6\text{CaO} : 3\text{SiO}_2$. He concludes that it is possible to improve the quality and to reduce the cost of production of glass simultaneously by the introduction of suitable quantities of alumina, but it is not at present possible to put forward a theoretical scheme defining the exact quantity. The limits to the use of alumina in glasses of different composition are variable, and the amount that would be necessary and beneficial in one type of glass might be detrimental in another. In every case, however, the beneficial effects due to alumina increase up to a certain definite point with increasing additions of alumina, and this point can be definitely determined for any type of glass. Further additions of alumina beyond this limit are detrimental in all cases.

⁸ Violet Dimbleby, F. W. Hodkin and W. E. S. Turner: The Influence of Aluminum on the Properties of Glass. *Jnl. Soc. Glass Technology* (1921) **5**, 107.

⁹ H. Hovestadt: Jena Glass and Its Scientific Uses. Translated by J. D. Everett and Alice Everett, London. (1902) 21.

¹⁰ S. English and W. E. S. Turner: The Effect of Aluminum on the Annealing Temperature of Glass. *Jnl. Soc. Glass Technology* (1921) **5**, 115.

¹¹ F. Singer: The Influence of Alumina on the Fusibility of Glasses. *Keramische Rundschau* (1917) **25**, 142. Abstracted in *Jnl. Soc. Glass Technology* (1918) **2**, 53.

Springer¹² was not able to verify all of Singer's results and found that alumina even in small amounts decreases the fusibility of a high alkali glass or a normal glass of the standard type, $.5\text{Na}_2\text{O} : .5\text{CaO} : 3\text{SiO}_2$, and retards fining. In the case of glasses rich in lime and correspondingly low in alkalis, however, he found that the addition of alumina did increase the fusibility and accelerated fining, and this within limits in proportion to the amount of alumina added. Springer concludes that the effect of alumina on the fusibility of a glass depends on many circumstances, but particularly on the composition of the glass, and cannot be stated as a fixed and definite rule.

Dimbleby, Hodkin and Turner¹³ found that moderately hard soda-lime glass was rendered more readily fusible by the addition of small amounts of alumina and that the glass of the percentage composition, SiO_2 , 74.13; Al_2O_3 , 2.67; CaO , 9.74; Na_2O , 13.54, melted and fined more easily than the corresponding lime glass without alumina.

According to Frink¹⁴ alumina increases the surface tension of the glass when chilled rapidly. This is beneficial in molding, as the glass will not take on the minor imperfections of the mold, and on the other hand, will still be sufficiently viscous to assume the general shape of the mold. Alumina is also believed by several observers to increase the tensile strength, hardness, and brilliancy of glass somewhat.

Frink states that glass cullet containing alumina does not mix well with other glass and, therefore, tends to produce cords or striae when used. He also holds that the viscosity of a glass is greater when the alumina content exceeds 3 per cent. Turner has also noted a greater viscosity in alumina-lime glasses as compared with lime glasses. Brockbank¹⁵ has called attention to the possibility that the blue color in the case of some glasses, where salt cake has been used in the batch, may not be due altogether to iron present as an impurity, but may be due to the formation of compounds of sulfur and alumina analogous in composition to ultramarine blue which consists of sodium, aluminum, silicon, sulfur and oxygen.

IRON OXIDES

Iron, either in the ferrous or ferric states, because of its coloring effect upon the glass, is the most detrimental impurity found in glass

¹² L. Springer: The Influence of Alumina on the Fusibility of Glasses. *Keramische Rundschau* (1917) **25**, 243. Abstracted in *Jnl. Soc. Glass Technology* (1918) **2**, 88.

¹³ Violet Dimbleby, F. W. Hodkin and W. E. S. Turner: The Influence of Aluminum on the Properties of Glass. *Jnl. Soc. Glass Technology* (1921) **5**, 107.

¹⁴ R. L. Frink: The Effects of Alumina on Glass. *Trans. American Ceramic Soc.* (1909) **11**, 99.

¹⁵ C. J. Brockbank: The Technical Control of a Window Glass Tank Furnace. *Trans. American Ceramic Soc.* (1915) **17**, 225.

sands. Ferrous iron imparts a green tint to glass, while ferric iron produces a yellow tint which is not nearly so noticeable. Since most glass is made under reducing conditions, the green color is the one usually developed. When the amount of iron present is small, this coloring effect can in part be overcome by the use of a decolorizer, such as manganese dioxide, nickel oxide, or selenium. According to Hodkin and Cousen,¹⁶ perfect decolorization is only obtained with glasses containing 0.09 to 0.1 per cent. of ferric oxide or less, those with higher amounts showing a loss of brightness, the depth of color being dependent upon the amounts of iron oxide and decolorizer present. This means that even if all other batch materials are pure, a condition extremely unlikely, a sand containing above 0.10 per cent. of ferric oxide will not give good colorless glass even when decolorized.

American glass manufacturers in recent years have been demanding an increasingly lower iron oxide content in the sands they use. The sands at present used in the manufacture of optical glass contain from 0.014 to .016 per cent. of ferric oxide, those used for chemical glassware below 0.02 per cent., while for good colorless bottles and containers the sand should preferably contain not more than 0.3 and should not exceed 0.04 per cent. Plate glass manufacturers employ sands containing from 0.05 to 0.15 per cent. of ferric oxide, although usually the percentage does not exceed 0.10. Some window glass manufacturers now demand sand containing less than 0.08 per cent. of ferric oxide. For ordinary green and amber bottles, sands containing from 0.3 to 1.0 per cent. or even more of ferric oxide can be used.

Iron may be present in the sand in the form of limonite, hematite, magnetite, ilmenite, biotite, hornblende, chlorite, or some other iron-bearing minerals. A little may also be introduced as metallic iron from the machinery used in crushing sandstone to sand. If it is present as limonite or hematite closely associated with kaolinite or clay, it may in large part be removed by washing. If, on the other hand, the limonite or hematite adheres closely as a coating to the quartz grains washing is of no avail. Metallic iron, magnetite and ilmenite can be removed from sand by means of a magnetic separator.

LIME

The amount of lime present in most American glass sands is so small that it has no detrimental effect upon the glass. All the common varieties such as bottle, plate and window glass contain lime as an essential constituent. A few glass sands in use at the present time contain as high as 1 per cent., or even more, of lime. Where this is compensated for

¹⁶ F. W. Hodkin and A. Cousen: *A Textbook of Glass Technology*. London (1925) 66.

in the batch formula, good results are obtained. When the lime content of the sand exceeds 0.5 per cent., it is exceedingly important that the amount does not vary very much from shipment to shipment for it is difficult for the glass manufacturer to adjust his formula for every new shipment of sand received.

MAGNESIA

Magnesia is much more apt to be introduced into the glass batch through the limestone used than through the sand. The composition of the former, therefore, must be watched with respect to this constituent. In the case of most American glass sands, the magnesia content is practically negligible.

When magnesia is added to a soda-lime glass,¹⁷ to replace the lime molecularly, a readier melting and easier working glass is produced, provided the amount of magnesia is kept below a certain limit. A glass containing 9.26 per cent. of lime will have a slower rate of melting and be more difficult to work than a glass with 6.43 per cent. of lime and 2.58 per cent. of magnesia or any intermediate composition between those limits. Beyond this proportion, however, further addition of magnesia becomes decreasingly beneficial and when the two oxides are together in equi-molecular proportions, as is the case when true dolomite is used, it is not as easy to melt as the corresponding lime glass and somewhat less easy to work. According to Hodkin and Cousen¹⁸ magnesia improves the lamp-working properties of lime-containing glass and diminishes the tendency to devitrification.

English and Turner¹⁹ have shown that magnesia, as compared with lime, tends to give a lower annealing point to the glass of which it is a component.

ALKALIES, ETC.

Alkalies enter into the composition of all ordinary types of glass and the minute traces occasionally present in the sand are not harmful. Titanium oxide probably rarely occurs in glass sands in sufficient amounts to have any detrimental effects upon the glass. It usually occurs in the sand as minute hair-like inclusions of rutile in the quartz grains themselves, although a little may also be present in the form of individual grains of rutile, ilmenite or titanite. Grains of zircon, which are occa-

¹⁷ Violet Dimpleby, F. W. Hodkin and W. E. S. Turner: Some Properties of Lime-magnesia Glasses and Their Commercial Application. Parts I and II, *Jnl. Soc. Glass Technology* (1921), **5**, 352.

¹⁸ F. W. Hodkin and A. Cousen: A Textbook of Glass Technology. London (1925) 109.

¹⁹ S. English and W. E. S. Turner: The Annealing Temperatures of Magnesia-soda Glasses. *Jnl. Soc. Glass Technology* (1919) **3**, 278.

sionally found in glass sands, are very undesirable on account of their refractoriness. They are apt to remain as stones in the glass. American glass sands rarely contain this mineral.

ORGANIC MATTER

Organic matter is occasionally present in small amounts in glass sands, either in the form of fragments of coal or as decayed vegetable matter. Some sandstones used for glass sand, such as those from the Pottsville formation of Ohio, Pennsylvania and West Virginia, sometimes contain thin streaks of coal which may not be entirely eliminated in the washing process. Unconsolidated surface sands may contain small amounts of decayed vegetable matter that are not entirely removed in the preparation of the sand for the market. Sometimes organic matter, such as coal, etc., is accidentally introduced into the sand during shipment and subsequent handling.

Sands used in the manufacture of lead glasses must be free from organic matter on account of the reducing action which it exerts upon lead compounds. Manufacturers of other high grade and special glasses made in pot furnaces also usually demand an absence of organic matter in their sand. In the case of glasses in which salt cake is used as a source of sodium, some form of carbon has to be added to the batch to enable the silica to decompose the sulfate.

Flint²⁰ in commenting on the influence of organic matter states that ordinarily 25 to 30 pounds of cullet are fed into the tank along with 100 pounds of batch. Two or three times in an 8-hour shift the floor around the machines is swept up and the cullet so gathered is fed back into the tank. This means that 200 out of several thousand pounds of cullet are covered with grease, oil, and sawdust. This would seem to indicate that in a glass tank a little organic matter is not necessarily harmful. It is partly taken care of by the use of small quantities of oxidizers, such as arsenic oxide or niter. A considerable portion of the carbonaceous matter is burned while riding on top of the batch and the rest is oxidized chemically.

SIZE OF GRAINS

Uniformity in size of grains is perhaps of more importance in a glass sand than the actual size of the grains themselves, although it is very essential that the sand be neither too coarse nor too fine. McSwiney²¹ has recently very ably discussed the effect of grain size in connection with the production of soda-lime glass. The process of glass production from the batch is conducted in three stages. First, the raw materials are

²⁰ F. C. Flint, chief chemist, Hazel-Atlas Glass Co. Private communication.

²¹ D. J. McSwiney: Effect of Sand Grain Size on Rate of Melting and Refining of Soda-lime Glass. *The Glass Industry* (1925) 6, 211.

heated to a temperature sufficiently high that the ingredients melt and react with one another to form glass. Then the temperature is raised somewhat to cause the glass to become more fluid, thus allowing the excess gases still held by it to pass off more freely. This is called the "fining" process. Finally, the glass is allowed to cool down to working viscosity.

The first two stages overlap one another. The first action that takes place is the combination of the soda ash and limestone with silica to form normal sodium and lime silicates. This reaction takes place on the surface of the sand grains. The carbon dioxide of the soda and limestone is liberated at this time and in part escapes and in part is retained until the "fining" stage is reached. All of the silica is not required to satisfy this reaction. Perhaps only two or three parts out of six are used in this way. The remaining three or four then slowly dissolve in or combine with the molten sodium and lime silicates. As the silica content of the resulting glass increases, its viscosity does likewise.

If the sand grains are too fine the first reaction will take place so rapidly that the large volumes of carbon dioxide liberated will cause the batch to foam badly and, in the case of a tank furnace, excessive amounts of material will be carried into the checkers of the regenerators and into the flues. Too fine sand may also be responsible for the formation of a fine persistent seed in the glass. According to McSwiney, this is not due primarily to the initial small size of the bubbles formed from the small sand grains, but to the fact that as the fine sand grains dissolve very rapidly, the increase in viscosity of the fluid medium takes place very rapidly. Because of this rapid increase in viscosity, the small bubbles subsequently formed do not have the freedom of movement or coalescence which they would otherwise have and cannot as readily escape from the glass. It might at first hand seem desirable that the sand should contain just enough fine sand to satisfy the first reaction between the soda ash and limestone. In practice, however, the use of cullet obviates this necessity as it contains enough silica to allow the formation of normal silicates.

Coarseness of Sand and Formation of Batch Scum

The coarser the sand used the greater is the tendency for the formation of batch scum. McSwiney, however, believes that it is possible to make good glass commercially from sand which is very much coarser than that ordinarily used, provided the operation is kept free from other factors which might cause scum formation. A sand containing only a few per cent. of coarse grains is more likely to cause scum, stones, and cords than a sand in which all the grains are uniformly coarse. If the sand grains are uniform in size, the attack on them will be approximately uniform and consequently they will decrease in size at a uniform rate. On the other

hand, if the sand is composed of a few per cent. of large grains and the remainder relatively small grains, the solution of the small grains will be completed before the large grains have decreased but very little in size. The solution of the large grains will then be taking place at a point where the solution speed is slowest because the solution will be near its saturation point in silica. The viscosity will be near the maximum so that diffusion and bubble movement will be very slow. If then the larger grains are not allowed for solution an amount of time much greater than the melt is usually given, they will remain undissolved as small stones or will agglomerate into a mass of scum, or, even if dissolved, the resultant high silica glass will remain incompletely mixed as small cords.

The finer portions of a glass sand are apt to contain a large part of the undesirable iron-bearing minerals of the sand, such as magnetite and ilmenite. Also, if the sand grains are coated with small amounts of limonite or hematite, the finer sand on account of its greater surface area in proportion to its weight will contain the higher percentage of iron. Several investigators²² have shown that the iron content of some glass sands can be materially reduced by carefully screening out the finer material.

The committee on standards of the glass section of the American Ceramic Society has proposed tentative specifications²³ in regard to grain size for glass sands. The sand shall be prepared so that the size of grains shall be rather uniform and be within the limits set in the following table:

Limiting Percentages of Various Sizes of Sand Grains

Through a No. 20 screen	100 per cent.
Through a No. 20 and remaining on a No. 40 screen . . .	Not more than 60 per cent. nor less than 40.
Through a No. 40 and remaining on a No. 60 screen . . .	Not more than 40 per cent. nor less than 30.
Through a No. 60 and remaining on a No. 100 screen . .	Not more than 20 per cent. nor less than 10.
Through a No. 100 screen	Not more than 5 per cent.
Screen tests shall be made with sand dried at 110° C., using United States Bureau of Standards standard screen sizes.	

The following screen tests on four typical washed and dried American glass sands were made by the writer in 1915, using a set of Tyler standard screen scale sieves:

²² Henry B. Kimmel and R. B. Gage: The Glass-sand Industry of New Jersey. Geol. Surv. of New Jersey, *Annual Report* (1906) 92. C. J. Peddle: British Glass-making Sands. *Jnl. Soc. Glass Technology* (1917) 1, 27.

²³ *Bull. American Ceramic Soc.* (1923) 2, 184.

Results of Screen Tests in Four Typical Washed and Dried American Glass Sands

	From the Oriskany sandstone at Maple- ton Depot, Huntingdon Co., Pa.	From the Oriskany sandstone at Vine- yard, Mifflin Co., Pa.	From the Pottsville sandstone at Kenner- dell, Venango Co., Pa.	From the St. Peter sandstone at Ottawa, La Salle Co., Ill.
Through 10-mesh and caught on 11			.42	
Through 14-mesh and caught on 20	.07	.05	.78	.04
Through 20-mesh and caught on 28	1 59	1 23	2 18	2.16
Through 28-mesh and caught on 35	13 11	4 88	7 28	19.81
Through 35-mesh and caught on 48	61 71	34 80	30 75	38 04
Through 48-mesh and caught on 65	20 25	41 03	37 06	14.19
Through 65-mesh and caught on 100	2 79	15 04	19 93	10 15
Through 100-mesh and caught on 150	.16	2 09	.85	6.66
Through 150-mesh and caught on 200	.03	.49	.10	3.68
Through 200-mesh and caught on pan	.01	.16	.03	4 76
		99 77	99 38	99 49

The amount of variation in size of sand grains is sometimes expressed in terms of a uniformity coefficient. This is the ratio of the size of grain which has 60 per cent. of the sample by weight finer than itself to the size which has 10 per cent. finer than itself. It can be obtained by plotting a curve on co-ordinate paper using the total percentages passing through the various screens as ordinates and the size of the openings in the screens as abscissas. A uniformity coefficient of 1 would mean that at least 50 per cent. of the sand was uniform in size, with not more than 10 per cent. smaller and 40 per cent. larger than this size. The term effective size is defined as a size such that 10 per cent. of the material by weight is composed of smaller grains and 90 per cent. of larger grains than this size. It is expressed in terms of millimeters. The effective size together with the uniformity coefficient define rather closely the size and uniformity of a sand.

In the case of the four screen tests given above, the one from Mapleton Depot has a uniformity coefficient of 1.40 and an effective size of 0.248 millimeters; the one from Vineyard, a uniformity coefficient of 1.59 and an effective size of 0.184 millimeters; the one from Kennerdell, a uniformity coefficient of 1.64 and an effective size of 0.180 millimeters; and the one from Ottawa, a uniformity coefficient of 3.16 and an effective size of 0.114 millimeters. The last one contains an excessive quantity of fine grains. If these had been removed, the uniformity coefficient would have been more nearly like that of the others.

In the preparation of glass sands, the coarser grains and the fine material can be readily removed by proper washing and screening. To re-arrange the percentages of the various grain sizes that constitute the bulk of the sand in a particular deposit so as to conform to a rigid set of specifications, however, is not an easy matter. While it can be done, it is not commercially feasible.

SHAPE OF GRAINS

The grains of water-laid glass sands, such as those of the Oriskany formation in Pennsylvania and West Virginia, shown in Fig. 1, the Pottsville in Ohio, Pennsylvania and West Virginia, and the unconsolidated sands of New Jersey, shown in Fig. 2, are irregular and usually angular in shape, while the grains of the St. Peter sandstone in Illinois and Missouri, shown in Fig. 3, and the Sylvania sandstone in Michigan, shown in Fig. 4, which were blown about by the wind for a long time before being deposited in their present positions, are more or less rounded in shape. All of the above sands have proved satisfactory in the manufacture of every type of glass for which they have been employed whenever they have been able to meet the necessary chemical requirements.

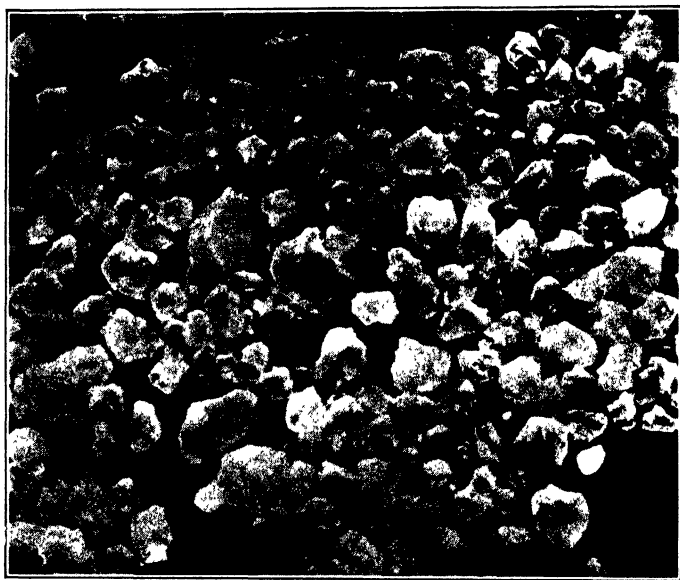


FIG. 1.—GLASS SAND WITH ANGULAR GRAINS, PRODUCED FROM THE ORISKANY SANDSTONE AT MAPLETON DEPOT, PA.

The fact that angular grains present a greater surface over which reaction can take place for a given weight of sand than rounded ones, and hence should go into solution more rapidly, has not been found to make any appreciable difference in actual practice. This factor probably enters in only at the start for as soon as reaction sets in the angular grains are soon rounded off. There is no longer very much prejudice on the part of glass manufacturers in favor of angular over rounded grains, provided the sand meets the necessary requirements in regard to chemical composition and grain size.

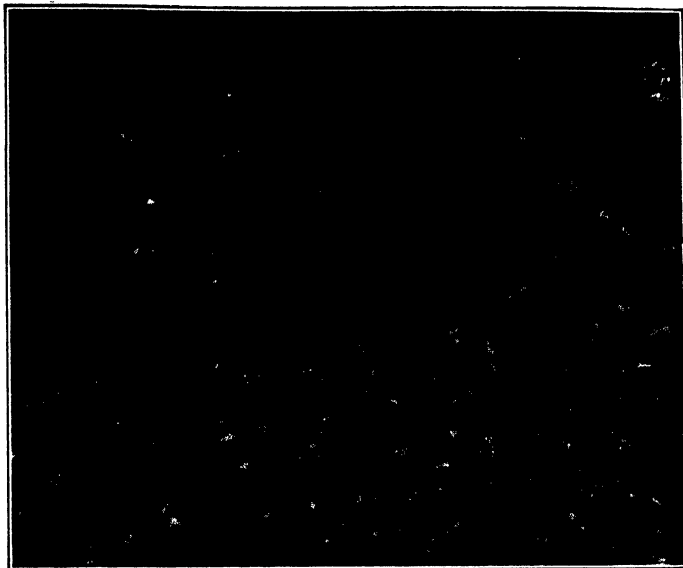


FIG. 2.—GLASS SAND WITH ANGULAR GRAINS, PRODUCED AT BRIDGETON, N. J.

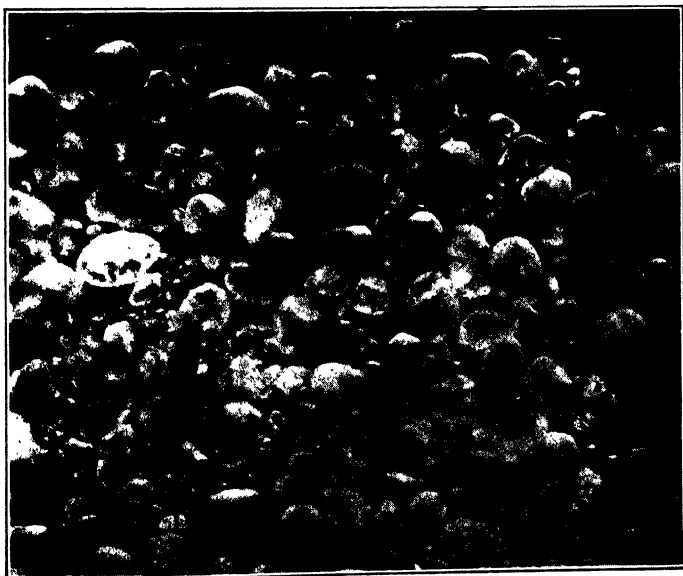


FIG. 3.—GLASS SAND WITH ROUNDED GRAINS, PRODUCED FROM ST. PETER SANDSTONE
AT OTTAWA, ILL.

SPECIFICATIONS

A few large glass companies own and operate their own sand plants. The bulk of the annual output of glass sand in the United States, however, is produced by companies engaged primarily in the sand business. In some cases, glass sand is their major product, although in most instances other types of sand are also produced from those portions of the sand that are not suited for glass making.

Very little glass sand is sold or purchased under rigid written specifications²⁴ at the present time. One large sand company operating in the

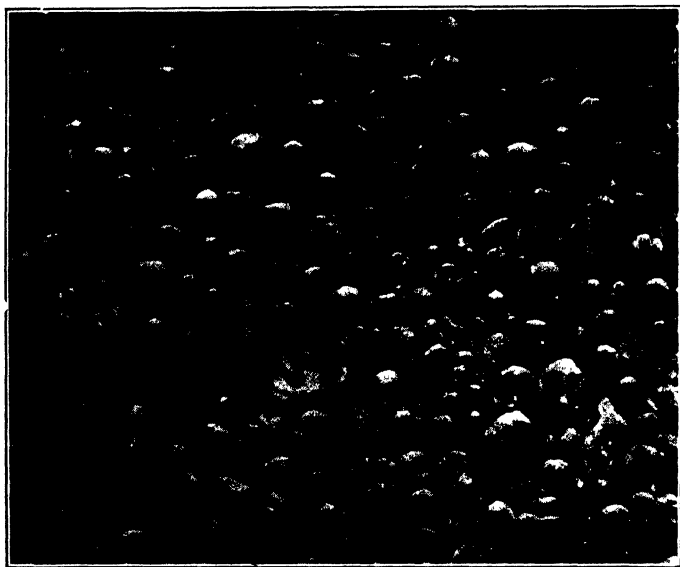


FIG. 4.—GLASS SAND, WITH ROUNDED GRAINS, PRODUCED FROM THE SILVANIA SANDSTONE AT ROCKWOOD, MICH.

Illinois district sells its sand under a guarantee that all its grains pass a 28-mesh and at least 98 per cent. remain on a standard 70-mesh testing screen, and that the ferric oxide content is under 0.025 per cent. Usually the glass manufacturer determines the type of sand which he thinks will meet his requirements and then buys from a producer who can supply him with that quality of sand in uniform and sufficient quantities to meet his needs at the lowest price, taking freight rates into consideration.

In recent years the demands of the manufacturers have become more stringent, particularly with reference to iron content. Optical glass manufacturers, necessarily requiring the highest quality of sand, insist

²⁴ Additional data for comparison may be found in a paper entitled "The Requirements of Sand and Limestone for Glass-making," by Ernest F. Burchard, U. S. Geol. Surv. *Bull.* 285 (1906) 452, and in the other Survey papers cited later.

on keeping the ferric oxide content down to 0.015 or 0.016 per cent. Each car received is sampled and analyzed for silica and ferric oxide. Manufacturers of good colorless bottles and glass containers usually insist on ferric oxide under 0.04 per cent. and in some instances under 0.03. Plate glass manufacturers sometimes use sands containing as high as 0.15 per cent. ferric oxide and 0.5 per cent. alumina, but prefer considerably lower limits. Some window glass concerns now demand that the ferric oxide content be kept under 0.08 per cent.

Uniformity in composition from shipment to shipment is of extreme importance and is usually insisted upon. Some glass sand producers make more than one grade of sand, the distinction being based largely on the ferric oxide content. These are sold to suit the requirements of their various customers. Most glass sand, including that employed for optical glass, is used at the glass plant as received from the producer. All glass sand must, therefore, be screened, washed, and dried before shipment, except where the natural conditions of the quarries allow the production by screening only of fourth, fifth, sixth, or seventh quality sand. Closed cars must be used for shipping first, second, or third quality sand and these must be thoroughly cleaned before loading and lined with paper.

MINING AND PREPARATION²⁵

West Virginia, Illinois, Pennsylvania, New Jersey and Missouri (in the order of 1923 output) produce most of the sand used for the manufacture of glass in this country. In 1923 their output comprised 83 per cent. of the total production.²⁶ In Pennsylvania and West Virginia the bulk of the glass sand produced is derived from the Oriskany sandstone. A little is prepared from Pottsville sandstones. In Illinois and Missouri practically all of the glass sand is derived from the St. Peter sandstone. In New Jersey the glass sands occur as horizontal beds of unconsolidated sand, and are sometimes 90 ft. thick and capped by from 1 to 15 ft. of gravel, sand and loam.²⁷ The Oriskany and St. Peter sandstones are the two major sources of glass sand in the United States.

²⁵ For further data on geologic relations and distribution of many American glass sands see the following papers:

"Glass Sands of the Middle Mississippi Basin," by Ernest F. Burchard, U. S. Geol. Surv. *Bull.* 285 (1906) 459.

"The Glass Sand Industry in Eastern West Virginia," by George W. Stose, U. S. Geol. Surv. *Bull.* 285 (1906), pp. 473-475.

"Glass Sand Industry of Indiana, Kentucky, and Ohio," by Ernest F. Burchard, U. S. Geol. Surv. *Bull.* 315, pp. 361-376.

"Notes on Various Glass Sands, Mainly Undeveloped," by Ernest F. Burchard, U. S. Geol. Surv. *Bull.* 315, pp. 377-382.

²⁶ A. T. Coons: Sand and Gravel in 1923. Mineral Resources of U. S., Part II (1923) 152.

²⁷ Henry B. Kümmel and R. B. Gage: The Glass Sand Industry of New Jersey. Geol. Surv. of New Jersey, *Annual Report* (1906) 80.

PENNSYLVANIA AND WEST VIRGINIA PRACTICE

Most of the Oriskany sandstone outcrop in Pennsylvania and West Virginia is valueless for glass sand either on account of its too high iron content or because it is still a hard, white to bluish-gray quartzite. Thus far, portions suitable for high-grade glass sand have been found and developed only in two main areas, one in the Juniata Valley region of

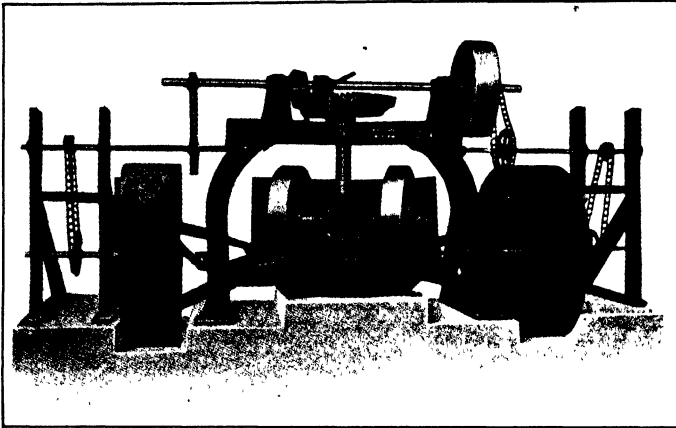


FIG. 5.—CHASER MILL AND SCREENS.

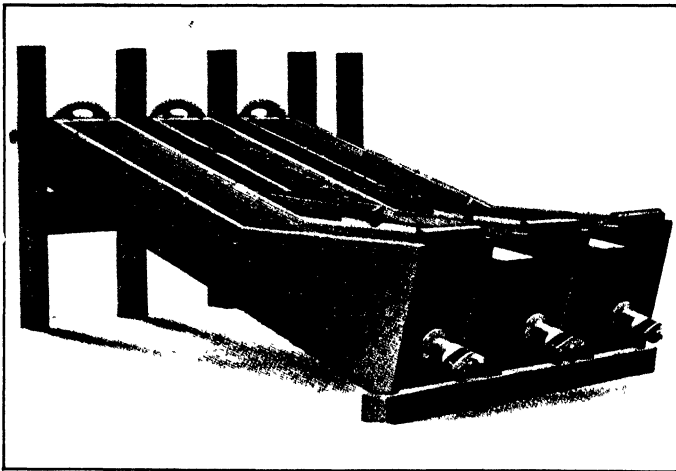


FIG. 6.—BATTERY OF THREE SCREW WASHERS.

central Pennsylvania, confined mainly to Huntingdon and Mifflin counties, and the other in northeastern West Virginia in Morgan County. In these two areas a very pure quartz sand was laid down during lower Devonian time which became consolidated into a hard quartzite. During the Appalachian uplift the beds were folded and by subsequent erosion

their bevelled edges have been exposed to weathering which in the areas mentioned has resulted in the partial and in places complete disintegration of the Oriskany into a friable sandstone, and in exceptional cases even into loose sand without the infiltration of any iron-bearing solutions. In these two areas the Oriskany sandstone yields some of the highest grade glass sand produced in the United States or any other country.

In Pennsylvania at present, the glass sand industry is most extensively developed in the vicinity of Mapleton Depot in Huntingdon County. The Oriskany sandstone outcrop here forms Rocky Ridge, a low ridge on the western flanks of Jacks Mountain. It varies in thickness from 130 to 170 ft. and dips from 60 to 65 degrees toward the westward. Mining is done entirely in open quarries, which are located along the ridge for a distance of about two miles to the north of the gap cut by the Juniata River through the ridge at Mapleton Depot and $1\frac{1}{2}$ miles to the south. The rock, while comparatively friable, has to be passed through jaw crushers and chaser mills to disintegrate it into loose sand. In the vicinity of Vineyard in Mifflin County some of the rock is so friable that after being loosened with light shots, a large percentage of sand can be recovered by hydraulic mining. A stream of water under pressure is directed against the sandstone face, breaking it up into loose sand which is washed into flumes and conducted to the sand plant. In the vicinity of McVeytown and Granville in the same county, extensive underground operations were formerly carried on. Here the sandstone is practically completely disintegrated into a loose exceptionally pure quartz sand which requires only washing, drying, and screening. A little is still mined at Granville. Only about 50 per cent. of the sand in the deposit is recovered by the method used.

In West Virginia, the most important center of glass sand production is near Berkeley Springs in Morgan County, where the Oriskany sandstone outcrop forms Warm Spring Ridge. The sandstone here ranges in thickness from 185 to 210 ft. and dips about 48 degrees toward the eastward. Mining is confined to open quarries, which are located along the ridge from a point about three-fourths of a mile south of the Potomac River for a distance of nearly three miles to Berkeley Springs. One quarry is also located near Great Cacapon on the west side of Cacapon Mountain. Warm Spring Ridge is on the east side.

QUARRY AND PLANT OPERATIONS

Quarrying operations in the Mapleton Depot and Berkeley Springs districts are carried on along the strike of the formation. A face, varying in width from 100 to 150 ft. at the base, is developed with walls on the footwall side of the quarry rising anywhere from 180 to 230 ft. in height. The slope of this wall is determined largely by the dip of the formation. The hanging wall side is always much lower. Sufficient sandstone is

usually left on the footwall to prevent the underlying calcareous shales from being washed into the quarry. Very little soil covers the sandstone. This is removed by stripping as the quarry face is advanced. The rock is broken down by blasting into suitable sizes for loading into small narrow-gage railway cars which are hauled by horses, mules or small locomotives to the crushing plant. Formerly, loading was done entirely by hand but now steam shovels mounted on caterpillar trucks are used in many of the quarries. These can handle much larger blocks but do not permit as careful sorting as is possible with hand loading.

At the plant the sandstone is crushed, washed, dried, and screened. The rock as it comes from the quarry is first passed over a grizzly consisting of a series of parallel steel bars placed about two inches apart on an incline. The oversize passes through a 12 by 20-in. Blake type jaw crusher which reduces it down to about a 3-in. diameter. Such a crusher handles from 14 to 25 tons of material per hour, depending upon the nature of the rock crushed. Where steam shovels have been introduced for loading, it has been found necessary to install larger jaw crushers, up to 40 by 42 in., to break down the big boulders to a size that can be handled by the smaller crushers.

The material from the jaw crushers and that which passed through the grizzly next goes directly to a chaser mill or grinding pan like that shown in Fig. 5. These mills consist of circular steel pans, varying in diameter from 6 to 9 ft., in which revolve two heavy steel rolls or mullers mounted on a horizontal axis. The pan itself is stationary. Water is fed into the pan and, as the material is crushed, it passes out through screens at the sides, two opposite ends of the pan being perforated for this purpose. The capacity of the mill varies with the diameter of the pan and the hardness of the material treated. A 9-ft. pan will handle anywhere from 100 to 250 tons per day of 10 hours, depending upon the readiness with which the sandstone crumbles under the mullers. For a 9-ft. mill, the rolls usually have a 12-in. face and weigh from 5000 to 6000 pounds each. The mullers revolve about a central vertical shaft at about 30 to 35 revolutions per minute.

SCREENING

From the chaser mill the sand goes to a revolving screen. Usually two of these are placed at opposite sides of the pan, as shown in Fig. 5. They have a diameter of from 7 to 8 ft. and a 24 to 36-in. face. They revolve about a central spindle at about 15 revolutions per minute. The screens are made of brass wire with usually 10 to 12 meshes per linear inch. The undersize material passes through the screens to the washers, while the oversize is returned to the chaser mill. Occasionally, when there is apt to be considerable coarse material present, the sand

is run through two of these revolving screens, the first one having only about 6 meshes per linear inch while the second has 12. This is done so as to protect the finer screen with the smaller diameter wire from too rapid wear by abrasion from coarse particles of rock.

From the revolving screens the undersize material goes to the sand washers. These consist of inclined wooden boxes or troughs, 10 to 12 ft. long and 18 to 22 in. wide on the inside. In these troughs are cast iron rotating screw conveyors which carry the sand from the bottom to the top. Fig. 6 shows their appearance. The washers are set up in batteries of two, three, four, five, and sometimes six—four being the usual number. They may be set up either parallel to one another, as shown in Fig. 6, or in tandem. The troughs are inclined at angles varying from 18 to 20 degrees from the horizontal. The sand enters each washer at the foot while clear water runs in at the head. The revolving screws carry the sand up the trough against the stream of water which carries away with it the clayey material and the excessively fine grains of sand. The dirty water overflows at the lower ends of the troughs into waste chutes. Where the washers are arranged in parallel, when the sand reaches the head of one washer it is dumped into a trough and is carried to the foot of the next by a stream of water. It passes on up this washer in a similar manner and thus on through the other washers of the battery. Where they are set up in tandem, they are so arranged that one discharges into the lower end of the next and so on through the series.

A plant with a 9-ft. grinding pan requires at least 150 gallons of water per minute. In some plants 400 to 600 gallons are used. An adequate water supply, therefore, is an absolute necessity for a washing plant of this type.

The sand from the washers is discharged onto a belt conveyor inclined at the end near the washers and horizontal at the end over the draining floor. It is installed near the roof of the draining shed so that the sand dropping from it builds up large cones reaching from the floor to the belt. The shed ordinarily has sufficient length so that by discharging at several points along the belt a number of cones of sand may be built up. A system of open joint tile drains under the floor permits the water to escape. The sand is usually allowed to drain at least 12 hours.

DRYING

Steam dryers are now employed at most plants, although a few direct heat dryers of the revolving cylinder type are still in use. Steam dryers are built in units, usually about 20 ft. long, 8 ft. wide, and 6 ft. high with hopper-shaped bottoms. The walls of the dryers are constructed of ordinary red brick. Inside are horizontal steam pipes

resting on inverted angle irons. These pipes are arranged in tiers, one above the other, and are placed closer and closer together toward the bottom. The sand is discharged onto the pipes, gradually drops down between them, and is finally discharged onto a belt conveyor at the bottom of the dryer. The steam and damp air from the sand accumulate under the angle irons on which the pipes rest and are drawn off by means of an exhaust fan. The sand is conveyed to the dryers from the drainage piles either by a belt conveyor which discharges over the dryers, or by an overhead travelling crane from which a grab-bucket is suspended. In the first type of installation the sand from the piles is usually shoveled by hand into a bucket elevator which discharges onto the belt conveyor. A steam dryer of the above type handles about 15 tons of sand per hour.

The sand from the dryers is next screened. Revolving screens or trommels are used. The size of screen openings varies in different plants, sizes from 14, 16, 18, 20, to 22 meshes per linear inch being employed. Eighteen meshes per linear inch is perhaps the most common size. In some plants the sand is passed over two screens, 14 and 18 or 20 and 22 being the combinations used. After the sand has been screened, it is elevated to the storage bins for shipment.

Electric power is now used at practically all plants. A fully equipped plant capable of producing 300 tons of sand per day and supplied with two units of machinery, including two 9-ft. chaser mills and one steam dryer, can be erected at the present time, in a location where the conditions are not unusual, for about \$80,000.²³ If an overhead crane for conveying the sand from the drainage piles to the dryer is included the cost is about \$15,000 more. The above estimate includes a substantially-built frame building, foundations for building and machinery, and the necessary electrical installations to operate the machinery. It does not, however, include outside power lines, railroad sidings, and quarry equipment. If only one dryer is installed, this has to be run day and night to give a 300-ton capacity.

GRADES OF GLASS SANDS

Three grades of sand are usually made in the Juniata Valley and Berkeley Springs districts. The sandstone is roughly sorted into different grades in the quarry on the basis of the amount of iron stain or limonite which it shows. Only the purest portions of the rock are used for what is called No. 1 sand. The bulk of this grade satisfies the specifications of the American Ceramic Society for first quality sand, with the exception that perhaps in most instances the alumina content is slightly higher, this usually ranging from 0.12 to 0.25 per cent. The iron content

²³ Private communication from a manufacturer of this type of equipment.

is frequently somewhat lower than the maximum allowed. The No. 2 sand contains a little more iron, but its ferric oxide content usually is also low, under 0.05 per cent. The alumina content is approximately the same as that of the No. 1. Very little of the No. 3 sand is sold for glass-making purposes. All of the No. 1 and that part of the No. 2 which is sold as glass sand is dried. The No. 3 is shipped wet.

At Mapleton Depot about 40 per cent. of the output is No. 1 sand; 48 per cent., No. 2, and 12 per cent., No. 3. In the vicinity of Vineyard, only about 22 per cent. of the output constitutes No. 1 sand, while 38 and 40 per cent. fall into the No. 2 and 3 classes respectively. At Granville, practically the entire product is of the No. 1 grade. In the Berkeley Springs district about 64 per cent. of the sand qualifies as No. 1, 30 per cent. as No. 2, and only 6 per cent. has to be sold as No. 3 grade.

At most places where glass sands are produced from Pottsville sandstone in Western Pennsylvania, the method of preparation is essentially the same as that described for the Oriskany sandstone. Sands equal in quality to the No. 1 grade from the Juniata Valley and Berkeley Springs districts, however, cannot be produced from Pottsville sandstone.

In the past, some of the cheaper grades of glass sand produced from the Pottsville were not washed. The sandstone was simply crushed to sand and screened. Very little glass sand of this character finds a market any longer. When this method of preparation is used, a dry grinding pan is employed. In a pan of this type, the mullers or rolls do not revolve about a central shaft although they turn about the horizontal axis on which they are mounted. The pan itself is rotated. The rolls tread on false plates, which may be removed when they are worn, while the outer portion of the bottom of the pan consists of screen plates through which the crushed material passes.

After the material has gone through the grinding pan it is conveyed to a revolving or shaking screen from which the undersize is conveyed to storage bins, stock piles, or directly to the cars, while the oversize goes back to the pan.

ILLINOIS

Practically all of the glass sand produced in Illinois is derived from the St. Peter sandstone, which crops out at a number of localities in the northern part of the state. Glass sand is obtained from it in Kendall, LaSalle and Ogle counties, with the largest production in the vicinity of Ottawa in La Salle County. The St. Peter sandstone ranges in thickness from 120 to 200 ft. in this district and lies almost horizontal. In many places it is a practically pure white quartz sandstone, the proportion of silica being very high, at some places exceeding 99 per cent., so that it is capable of yielding an excellent quality of glass sand comparable with that derived from the Oriskany sandstone in Pennsylvania.

and West Virginia. It is usually so poorly cemented that the rock crumbles readily. The rounded character of its grains has already been mentioned.

At one large plant the following method of mining and preparation is used.²⁹ Light shots of slow-burning dynamite are used to disintegrate the rock. The sand is then hydraulicked to a sump from which it is pumped in suspension in water by means of a sand pump to the foot of a drag conveyor that elevates it out of the quarry to the top of the washer.

The washing plant contains two large concrete bins of oval shape, each of which is supplied with numerous jets of clean water that serve to agitate the sand. The fine material rises to the surface and is carried off in suspension over a skimming dam in the side of the bin, which is raised as the bin fills with sand. From the washing bins, the sand is again pumped in suspension in water to draining bins. There are 12 of these concrete bins of 200-ton capacity each, with hopper-shaped drainage bottoms and the same skimming arrangement on the sides as the washers. Doors are provided in the sides of the draining bins from which the sand is delivered to steam dryers. A belt conveyor underneath the dryers carries the dry sand to an elevator that raises it to the top of the screening and storage building. Inclined vibrating screens and vibrating separators are used for classifying the sand into four different products, one of which is sold as glass sand.

All of the glass sand produced at this plant is guaranteed to pass a 28-mesh and at least 98 per cent. to remain on a standard 70-mesh testing screen, as well as to have a ferric oxide content under 0.025 per cent. Much of it averages about 0.020 per cent. and some of it has run as low as 0.014 per cent. The untreated sand contains about 0.043 per cent.

MISSOURI

The St. Peter sandstone is also the source of the glass sand produced in Missouri at the present time. Most of the production is confined to Franklin, Jefferson, St. Charles, and St. Louis counties in a district lying to the west and south of the city of St. Louis. In this area the sandstone has a thickness ranging from 60 to 100 ft., but the entire thickness is rarely available for glass sand. As a rule, only portions of it can be utilized. The dip of the formation ranges from about $\frac{1}{2}$ to 20 degrees to the northeast.

Mining of the St. Peter sandstone in Missouri is done both by open pit and by underground methods.³⁰ In the quarries there is usually an overburden consisting either of loess or of limestone or often of both,

²⁹ Private communication.

³⁰ C. L. Dake: *The Sand and Gravel Resources of Missouri*. Missouri Bur. Geol. and Mines (1918) 15, 2nd series, 39.

which varies from a few inches to 30 ft. or more in thickness. When the covering is of limestone, shooting is invariably part of the stripping operation. In most of the quarries the sandstone is sufficiently cemented to make blasting necessary. The sand is shot down into great piles either of broken blocks or of loose sand, depending on the degree of cementation. This is loaded into quarry cars either by hand or by the use of steam shovels. Mules, cable, gravity, or electric-motor haulage are used. At a few places, where the overburden is particularly heavy, underground mining methods are resorted to. Usually about 25 per cent. of the sandstone has to be left in the form of pillars.

Crushing is generally required. At a few places the rock is so friable that the simple washing through a coarse revolving screen is sufficient to cause it to crumble to loose sand. In most places, however, regular crushers are employed. Gyratory crushers and hammer mills are the most popular types.

In 1918, only two plants operating in the state washed their glass sand. The washing process consists in passing a mixture of sand and water over riffles, or through successive settling tanks where the coarse material settles and the finely divided limonite and clay, together with much undesirable fine quartz, are floated off with the water. The washing usually gives an appreciable reduction in alumina and ferric oxide. One company reduces its quarry-run sand from 0.210 per cent. alumina to 0.049, and the ferric oxide content from 0.075 to 0.031. At plants where the sand is washed it is usually screened twice, once through a coarse screen after crushing, the oversize being returned to the crusher, and again after it has been washed and dried when it is usually passed through a 20-mesh screen. Both the direct heat rotary and steam types of dryers are used.

NEW JERSEY

The New Jersey glass sand deposits occur as practically horizontal beds of unconsolidated sand sometimes reaching thicknesses up to 90 ft., which are capped by layers of gravel, sand, and loam, varying in thickness from 1 to 15 ft. While the New Jersey glass sands are not of as high quality as the best grades that are produced from the Oriskany and St. Peter sandstones, they are of sufficient purity to be used in the manufacture of high grade bottles, pressed ware, and window glass.

Mining is usually done with steam shovels if the deposit is above water level and will not hold water for a dredging pond.²¹ If a pond can be made, the mining is done by hydraulic dredging with centrifugal pumps placed on a floating dredge and discharging to the washing and screening plant through long pipe lines.

²¹ W. M. Weigel: Sandblast Sand. U. S. Bur. Mines, *Reports of Investigations*, Ser. No. 2615 (1924) June.

Some type of washing is carried on in all cases. Where the sand is particularly clean only screen washing may be resorted to. At some plants screw washers of the type already described are used. Both stationary steam dryers and direct heat rotary dryers are employed for drying the sand. The coarser material is usually taken out by revolving screens while the fine material is separated on shaking or vibrating screens.

PRICES AND PRODUCTION

In 1923, only 1.4 per cent. of the total sand and gravel produced in the United States was sold for glass-making purposes but, on account of the higher price that glass sand commands as compared with other types, its value represented 4.1 per cent. of that of the total output.³² West Virginia, during that year, produced 25 per cent. of the total output; Illinois, 24; Pennsylvania, 17; New Jersey, 9; and Missouri, 7 per cent. The average price per ton received for the total output of the United States during that year was \$1.84; for West Virginia, \$2.30; for Illinois, \$1.57; for Pennsylvania, \$2.06; for New Jersey, \$1.64; and for Missouri, \$1.40.

The glass industry of the United States is well located with respect to the above sources of sand. Sixty-two per cent. of the total value of the glass produced in 1919³³ came from factories located in the above five states and the major portion of the remainder came from adjacent states. The reserves of high grade glass sand in the Eastern United States and the Mississippi Valley region are large. On the Pacific Coast, however, no deposits capable of yielding a good quality of glass sand have thus far been discovered. Some of the California glass plants import Belgian sand. During 1924 this amounted to 5775 long tons. The sand is brought into the California ports as ship ballast and hence is sold at a very low price.

DISCUSSION

F. A. WILDER, North Holston, Va.—Is it altogether out of the question to use quartzite? I ask because in Southwest Virginia we have quartzites that analyze 99 per cent. silica, with satisfactory iron content, and they are being used in a small way now, I understand, for glass sand purposes. Power is relatively cheap and the material lies high above the drainage line, so that we are not troubled with water in the operations. For glass purposes in the South the freight haul is a factor, when you consider taking material from Illinois and West Virginia.

³² A. T. Coons: Sand and Gravel in 1923. Mineral Resources of U. S., Part II (1923) 152.

³³ Fourteenth Census of U. S., 1920 (1923) 8, 388.

C. R. FETTKER.—There are two reasons why quartzite is not desirable: First, the additional expense of crushing such material to the necessary size; and second, the rather excessive amount of fine material produced in order to reduce the bulk of the product to the required size.

There have been several attempts made to use quartzites. I know of one instance in West Virginia, and one in Pennsylvania. Both were failures. They had difficulty in making the right-sized material at a cost to compete with sands derived from more friable sandstones. In California I understand they have tried unsuccessfully to use massive quartz which occurs comparatively pure in the form of large veins in some localities. Of course, they can import foreign sand at a comparatively low figure on the Pacific Coast. This is mostly Belgian sand, and is brought in as ballast.

Washing and Sizing Sand and Gravel

BY EDMUND SHAW,* CHICAGO, ILL.

(New York Meeting, February, 1926)

IN THE year just past there were produced in the United States about 170,000,000 tons of sand and gravel. Much of this was pit-run material used for gravelling roads and as railroad ballast on lines that did not carry heavy traffic. But more than half of it was marketed as washed and sized, or graded, material.

The methods used for preparing sand and gravel for the market have long been used in ore dressing and, as in ore dressing, depend on differences in the specific gravity of two substances or in the size or weight of particles. But many changes in the design and operation of plants and machines have been necessary. In ore dressing, the concentrate is only a small part of the feed; in sand and gravel washing, it is much the larger part of the feed. In addition, such close work as is needed when concentrating a metallic ore is not needed when washing gravel; the ability to put through a large tonnage is more important, and sizing, which is only a preliminary process in ore dressing, is an end to be attained.

Rock crushers are found in most sand and gravel plants and they are used to break up the larger pieces from the deposit (known as boulders and cobbles) which are removed by a scalping screen. The crusher discharge is usually sent back to the scalping screen, the perforations in this screen setting the maximum size of the finished product.

WASHING

Washing is to prepare sand and gravel so that they may be used as aggregates in concrete and wall plaster and in various processes in which impurities would harm the product. At one end of the scale of washed materials may stand ordinary concrete sand, which in some states may contain as much as 3 per cent. of clay and still be used in highway concrete construction. At the other end will stand the silica sand used for making plate glass, which must be washed so clean that the impurities that can be removed by washing do not exceed a few hundredths of a per cent. The methods and machinery that would produce one of these

* Editor, *Rock Products*.

would not produce the other. However, the theoretical principles of washing are the same for both materials.

Washing and sizing are generally carried on at the same time and in the same equipment, but the two are distinct processes. It is possible to wash first and to size afterward, as is customary for the production of blast sands, filter sands, and the like. And it is important to understand that the two processes are separate, for mistakes in design and in plant operation have come from confusing the two. In general, whatever improves the washing improves the sizing. Thus, the use of a large amount of water improves the washing and it also carries the material through the screens at a faster rate. At some plants where the material dug from the bank is clean enough to pass specifications, water has been used because of the greater output of screened materials that could be secured.

The word *sizing* has been used in preference to *screening* because only a portion of the product is sized by screens. The greater part of the separation of sand into sizes is by means of hydraulic classification. This is employed both as a washing and a sizing method.

IMPURITIES TO BE WASHED OUT

The materials that must be washed from sand are divided into the soluble and insoluble substances, and the organic and inorganic substances. The solubles to be removed are mainly tannic and other organic acids that greatly affect the strength of concrete when present in even minute amounts. Sand and gravel containing these are not found in all parts of the country; but in some sections, as in some of the southeastern states, they present a serious problem to the producer. Fortunately they can be readily removed by washing, provided a supply of clean water is obtainable. The only soluble mineral substances that must be removed are the sulfates, found especially in the arid parts of the country. It is sometimes difficult to remove these because the water supply in such districts is apt to be limited or to be contaminated with sulfates, the so-called "alkali" waters.

The insoluble substances to be removed are, first of all, clay, which is present in almost every deposit. It occurs: first, as soft clay, which has been carried into the deposit by rains or has come from the decomposition of some of the minerals in the deposit; second, as film clay, coming from the decomposition of the minerals and existing as a film on the outside of the grains and pebbles; and third, as a very hard clay, which forms clay balls almost as hard as the softer pebbles. Soft clay is easy to wash out, film clay may be scoured off by scrubbers, but clay balls are difficult to remove and special machines must be used when they are present. Loam which comes from the overburden of the deposit may be removed as easily as soft clay and by the same methods.

Next often found are the organic impurities, which consist of sticks, bark, and leaves and the roots of grasses, shrubs, and trees, all of which may be quite easily removed. Lignite and coal form another class of the organic impurities and their removal is more difficult; however, it is being accomplished on a commercial scale.

Of the inorganic materials, the most difficult to remove is shale. Its removal on a commercial scale is an unsolved problem, but experiments, carried on for two years by C. S. Huntington for one of the largest machinery houses, have shown so much promise that we can say that some of the shaly gravels can be sufficiently cleaned for use as concrete aggregates. The objection to shale is not altogether due to its softness; some kinds of shale absorb water and swell while concrete is setting and hardening, and hence tend to disrupt the concrete.

Other deleterious mineral substances are slate, mica, pyrite, and "sand rock," which is the name given to soft sandstone. These are all difficult to remove and deposits containing much of anyone of them are not considered workable on a commercial scale. Mica can sometimes be removed by classification sufficiently to permit the sand to be used for making concrete.

The oxidized forms of iron ore do not detract from the value of sand except for making glass. Glass sand is often concentrated on tables to remove iron minerals. Pyrite is not often found in natural sands but it is said to make trouble in artificial sands, such as the tailings from ore-dressing plants, which are sometimes used in making concrete.

STANDARD WASHING METHOD

While the same method of washing will not do for the removal of all these substances, as they differ so much, there is a standard method of washing that will remove soft clay and the organic acids; and it is to apply this method that the ordinary sand and gravel plant is designed. This method employs a combination of washing by filtration and washing by decantation.

Washing by filtration is applied to the coarser sizes (gravel) and usually the material is screened at the same time. The revolving screen, or trommel, is generally used; it has held first place in sand and gravel preparation more because it is a good washer than because it is a good screen. Considerable water is put into the screen with the gravel, or mixture of gravel or sand, at the first screen and as this water passes through the screen it carries most of the clay and the sand, which are separated later. To remove the last of the clay from the gravel, sprays are used farther along in the screen. Where a series of screens are used to make a series of sizes, each screen has its own spray for rinsing, so that very clean material is produced if enough water is used.

This method is economical of water, for water is most economically applied in washing where it can be run on the material in a succession of washes, each displacing the other, which is the ordinary method used in the laboratory for washing out a filtrate. But it cannot be applied to the finer sizes, the sands. Any filter with small enough meshes to hold back the finer grains of sand soon clogs either with sand or with clay and the working comes to an end. Hence sand is always washed by decantation.

Those who are familiar with cyanidation and similar hydrometallurgical processes understand the theory of the removal of a soluble substance by repeated decantations. The principles involved in sand washing are the same. The clay, which is really in suspension, may be considered as a salt in solution and its removal will then be according to the same laws. In brief, the percentage of clay removed and the percentage left with the sand are proportional to the water removed and left with the sand. Thus, it is possible to calculate the amount of water required for washing sand, provided the percentage of clay is known.

The apparatus by which washing by filtration and decantation are applied varies according to the ideas of the plant designed. The most popular form of screen, used for both washing and screening, is the conical trommel. A number of these are fastened to a common shaft, which is set at about 22° from the horizontal so that the material will flow readily from one screen to another. The first usually has $2\frac{1}{2}$ -in. holes; the second either $1\frac{1}{2}$ - or $1\frac{1}{4}$ -in. holes; the third $\frac{5}{8}$ - or $\frac{1}{2}$ -in. holes, and the last screen in the series, known as the sand screen, has holes that may be anything from $\frac{7}{32}$ to $\frac{3}{8}$ in., the larger size being more commonly used. Each screen is provided with chutes so that the oversize is sent to a bin and the undersize is sent to the screen ahead, except in the case of the sand screen, from which the undersize goes to be washed by decantation. Each of these screens has its own washing spray, which is usually a perforated pipe connected to pressure water.

One disadvantage of this system is that it requires considerable space both vertically and horizontally. For this reason jacketed screens are used in plants where it is desirable to save space; the inner jacket or main section has $2\frac{3}{4}$ -in. holes and the others successively smaller holes to the sand-screen size. No more than three jackets are usually combined in this way. If another screen is needed to make a finer product than that made by the outer jacket of the main screen, it is mounted separately.

Some of these jacketed screens are especially designed for washing. They have tire and trunnion bearings at both ends and are driven by a gear that goes around the main section. This leaves everything clear inside so that a 4- or 6-in. pipe can be passed through to supply plenty of water for the sprays. Such screens are very long, 24 ft. being a common length for a 48-in. screen.

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Another type of screen, which was designed to be a good washer, is a conical screen set on a horizontal shaft with the small end closed. The feed into the screen and the discharge out are both at the large end, the feed being carried in through a launder above the center. Jets of water under heavy pressure play on the mass of material where it turns in the screen and disintegrate lumps of clay and wash the pebbles clean.

WASHING SAND BY DECANTATION

The settlers, in which sand is caught and washed by decantation, are mainly of the continuous-discharge type. Considered as classifiers, most of them belong to the surface-current type, the current passing from end to end, so that the sand drops out as a roughly graded product, the coarser sand being nearest the entrance point. Valves at the bottom permit the discharge of the settled sand as a quicksand flow. The moisture contained in the voids of such a discharge is about 27 per cent. for ordinary concrete sands.

A large number of plants use a device in which the discharge of sand is automatically controlled. These work in various ways. In one form, the oldest of all, the weight of the settled sand tilts the box when it reaches a certain depth and this tilting causes the valve to open. In another, the weight of the sand carries the whole settler down, as it is hung on a lever and balanced by a counterweight; this causes the valve to open. In still another, the settled sand obstructs the inflow of water, when it reaches a certain height, and causes it to flow into a chamber in which there is a float that opens the valve. These automatic sand settlers, in general, give a much cleaner product than settlers with hand-operated valves. For one thing, conditions of settling are kept constant; and for another, the danger of the attendant forgetting to close a valve in time and allowing a lot of clayey water to run into the sand is obviated.

WATER REQUIRED FOR WASHING

The amount of water required for washing will usually be governed by the amount that is needed to wash the sand by decantation. This can best be illustrated by an example. Suppose that the bank run contains 15 per cent. clay and that the proportion of sand to gravel in the remainder is as 3 is to 2, which is a proportion commonly found. Then each ton of bank run will contain:

	Pounds
Clay, 15 per cent.....	300
Sand, three-fifths of 1700 lb.....	1020
Gravel, two-fifths of 1700 lb.....	680

2000

Assuming that the clay must be not over 3 per cent. in the sand product, the 1020 lb. of sand will be 97 per cent., which gives the weight

of the clay with the sand as 31.5 lb. As the weight of the clay removed is as the weight of the water removed, we have the proportion $268.5 (300 - 31.5):31.5 = x:377.2$. This last figure is the water that will remain with the sand if the mixture contains 27 per cent. moisture. Solving this, we find 3212 lb. of water is required to remove the clay so that the sand recovered will not have a clay product greater than 3 per cent. To this must be added the water remaining with the sand (377.2 lb.) and the water lost in rinsing the gravel, which will be at least 25 per cent. of its weight or 170 lb. The total will, therefore, be 3759 lb.; and as at least 10 per cent. must be added for safety, 4135 lb. is the minimum that can be used. This is a ratio of 2.07 to 1 or 2.4 to 1, figuring the ratio on the finished product, as is the usual practice.

A rough rule used by producers for the minimum water required is 1 g. p. m. for 1 ton per 10-hr. day of finished product. That is, to wash 1000 tons per day a plant would need 1000 g. p. m. of water. This is a ratio of 2.5 to 1. But the plants that can get along with any such theoretical ratio are few. The feed to the plant is apt to be uneven in quantity and un-uniform in the proportion of sand to gravel, and enough water must be provided to take care of the worst condition. Supposing that all the feed was sand with 15 per cent. clay (temporarily), the water needed would be 6265 lb. for that time, which is a ratio of 3.7 to 1. Ratios of 3 or 4 to 1 are not uncommon. The highest ratio noted by the writer is 7 to 1, but this was needed because of the unusual amount of clay that had to be removed, nearly 50 per cent. of what was excavated from the bank being wasted as clay and fine sand.

UNIFORM FEEDING

The foregoing illustrates another point in washing, that is, the necessity for a uniform feed to the plant if water is to be used economically and clean products made. The older sand and gravel operations used to pick from the bank according to the market, drawing heavily on the sandy portions when sand was in demand and heavily on the gravelly portions when gravel was in demand. The later practice is to work the bank as a whole and to draw evenly from all parts, storing that part of the product which cannot be sold at once. This has resulted not only in better products but in better deliveries and an even operation of the plant throughout the season. The cost of storage is more than made up by the ability to keep that plant running steadily and to fill large orders promptly.

SPECIAL WASHING METHODS

What has been said so far refers to the removal of soft clay. Where firm clay is present, the same plant will serve with the addition of a scrubber. The commonest form of scrubber is a cylinder 4 to 6 ft. in diameter

water. The other is to set the screen at a 45° to 60° angle and to feed the pulp against it. Both methods work well. The flat screens are much used in dredging operations, where there is an abundance of water and where saving height is desirable.

Gravity screens are sometimes used as a preliminary screen to take out a large part of the sand and water before sending the gravel to be carefully sized. This relieves the work of the sizing screens and makes a better separation possible. In one large plant near New York, all the material from the bank is first passed over gravity screens to take out the greater part of the sand. A sand screen follows the gravel screens but it is not crowded.

Revolving screens have been favored because they are good washers. The objection to them is that they blind easily, the centrifugal force present tending to drive the pebbles and grains into the perforations. Various devices are used to keep the meshes open, the most used form being a roller hung in loose bearings so that it can always rest on the screen. The weight of the roller pushes the pebbles out of the holes in which they are stuck and sends them to the oversize where they belong. Perforated plates with round holes are almost always used as the screening medium.

Shaking screens are not used so much. They are efficient but when they are made in the large sizes, which have been tried on big tonnages of sand and gravel, they communicate a strong shake to the building. They are also hard to keep in repair. The smaller sizes are not hard on the building and when they are set to balance so that one shakes out while the other shakes in, they are not objectionable and do good work.

Vibrating screens are coming into use more and more, especially for separating the finer sizes. There are several of these on the market and all are efficient. Most of them vibrate the whole screen and the frame that holds it, and many ingenious methods have been devised for minimizing the effect of vibrations. The later models are especially good in that respect.

The screens that vibrate the fabric are a comparatively recent development but their success has been great. They are especially used on the finer sizes but they may be employed on the coarser sizes and for either wet or dry screening.

CLASSIFICATION

Sand is sized either by screening or classification. As a result of the improvements of the last five or ten years in fine screens, the tendency is to screen rather than to classify. Classification demands a steady feed of both solids and water to do good work and this is often hard to obtain when running a commercial sand plant.

As about every form of classifier that could be devised has been tried out in ore dressing, no new forms have come from sand and gravel practice. The improvements made have been largely toward increasing the tonnage through the machine.

Of mechanical classifiers, the rake (Dorr) classifier and the chain-and-belt drag classifiers are standard and largely used. The sand wheel is just beginning to be used and will probably find a larger use in time. Dewatering elevators are employed to some extent.

Of hydraulic classifiers, the surface-current is perhaps the most used. The old type of sand box is generally run as a surface-current classifier.

Rising-current water and hindered-settling classifiers have not been much used, but probably as the demand for cleaner sand increases, more of these will come into use.

FUTURE OF THE INDUSTRY

The production of washed sand and gravel is increasing and probably will continue to increase. Methods and machines are improving. The cleaner deposits of material are becoming exhausted and producers are beginning to work those deposits of material that must be carefully and thoroughly washed to make a marketable product. Almost all large plants are now in charge of men with engineering education. Some of these are graduates of schools of mining engineering, but many of them are civil engineers who got into the business through their knowledge of the product gained in road building and general contracting work.

Preparation and Use of Industrial Special Sands*

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(New York Meeting, February 1926)

DEFINITION OF SPECIAL SANDS

THE general term "sand" applies to a multitude of similar materials consisting of fine granular mineral. As usually understood, it means the ordinary natural product used for structural purposes and made up largely of grains of quartz. Quartz sand constitutes by far the greater bulk of the production, but there are other grades used for industrial purposes, such as molding sand, glass sand and many others, that may be grouped under the general name of special sands.

Under this general group would fall filter sand, sand-blast sand, engine sand, potter's sand, abrasive sands of all kinds, sand for pulverizing, roofing sand, flooring sand, fire or furnace sand, standard sand, burnishing sand, sand for magnesium oxychloride cement-plasters and sand for chemical and metallurgical purposes.

SOURCES OF SUPPLY

Sand is a widely distributed natural product and even the better grades are low-priced commodities. For these reasons development has occurred near points of consumption where sand meeting the requirements is available. Some special grades, however, cannot be prepared from any sand bed and shipments are often made over considerable distances when the only developed deposit is remote from the consuming center. This is true of filter sand, sand-blast sand, sand for pulverizing and some of the others when chemical purity or grain size, coupled with the need of a properly equipped plant for preparation, are required.

New Jersey is a large producer of filter, engine, sand-blast, fire, and pulverizing sand. Pennsylvania, and West Virginia produce special sands for pulverizing, fire sand, abrasive sand, engine sand and sand for chemical and metallurgical use. Ohio produces much sand-blast, fire and abrasive sand, and some filter sand. Illinois and Minnesota produce

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filter sand, sand-blast sand, abrasive sand, fire sand, sand for pulverizing and for chemical and metallurgical use. Standard sand is prepared at Ottawa, Ill. Missouri produces considerable quantities of abrasive sand, fire sand, engine sand and some filter sand. Some or all of the special sands are produced in many other States but those named are the centers of production and, it will be noted, they are near the chief industrial districts of the Eastern and Middle States.

There are undoubtedly deposits of sand in the Southern and Western States from which special sands may be prepared whenever the demand arises.

MINING METHODS

Most sand deposits are unconsolidated and methods of mining or excavating special sands do not differ from those used for structural sands. If the deposit is under water or can be flooded, excavation by suction dredge seems to be efficient and the most popular. If coarse gravel predominates and the demand and reserve warrants the capital outlay, ladder dredges are used, or sometimes clam shells. Steam shovels and drag-line excavators are in common use for dry sand banks.

Consolidated deposits such as those in the Mapleton, Pa., Berkeley Springs, W. V., Portage and Massillon, Ohio, and Ottawa, Ill., are mined by open cuts. In Pennsylvania and West Virginia the soft sandstone beds are tilted at a high angle. Here tripod and jackhammer drills are employed for comparatively shallow blast holes and usually the rock is loaded by hand. At Portage, Ohio, a consolidated gravel and coarse sand is drilled by churn drills to the depth of the face, 15 to 60 ft., and several holes are blasted at once. Loading here is by electric shovel.

In the Ottawa district, the St. Peter sandstone, the source of the sand, lies almost level and the sand is only lightly consolidated. Blast holes are put down by a hydraulic jet, the tip of which is fitted with short cutting edges or wings. Only enough explosive is used to loosen the sand, which is then washed down from the face by a hydraulic giant and pumped to an elevator that raises the sand to the treatment plant.

In Missouri, in the vicinity of Pacific and Crystal City, sand is mined both underground and from open excavations. At Crystal City the Pittsburgh Plate Glass Co. obtains both its glass sand and abrasive sand for grinding the glass from the same mine. The output is simply divided: part going to the washing and preparation plant for glass sand and the remainder sent to the tanks for grinding sand.

PREPARATION

Nearly all special sands must be clean and free from excessive fines and clay coating. This means that they must be washed and a suitable supply of water for this purpose is required. In some plants the entire

output is one or more grades of special sands and the treatment then resolves itself into washing followed sometimes by drying and screen sizing. Hydraulic classification is not used for the separation of closely sized sands.

At many plants the special sand produced is only a byproduct. For example, some plants that ship glass sand as their main product, also make sand-blast, filter and abrasive sand and sand for pulverizing. Some plants that produce steel-molding sand or commercial gravel-and-sand, also produce several grades of sand-blast and filter sand. The size of the natural sand grains and the mineralogical composition, of course, limit the special sand that can be prepared.

Washing.—Unconsolidated sands are washed in the ordinary way by means of scrubbers, screens and settling tanks. If the main production must be unusually clean, as for glass sand, more thorough washing is given. At some plants in New Jersey a series of chain drags is used in standard practice. Consolidated sands, as in the Mapleton, Pa., and Berkeley Springs, W. Va., districts, require crushing, which is followed by wet grinding in modified chaser mills and washing by counter-current flow in helical screw washers of the Lewistown type. It would seem that more efficient grinding machines than the chaser mills could be used, but undoubtedly the scouring action, due to the sliding of part of the roller on the track, has an important effect in removing the clay coating from the sand grains. So far no satisfactory substitute for the chaser mill has been developed.

In the Ottawa district, crushing and grinding is unnecessary as the hydraulic giant and subsequent pumping and washing separate the loosely cemented grains. Washing is done in tanks arranged with an overflow. Sometimes also hydraulic water flowing upward from the bottom of the tanks is used. The practice at Crystal City, Mo., is similar except that the sand is disintegrated in a steel-plate cylinder like a revolving screen with the discharge end closed. The lumps of sandstone act as pebbles and crush themselves until fine enough to pass the 1-in. openings in the shell. The resultant material is passed through a wet-crushing hammer mill.

Two methods, or slight modifications of them, may be used to treat the wet washed sand: First, either the total amount passing through the plant is separated into the respective sizes, or a fraction of the total amount is split off and so separated, or, second, a part of the sand between certain maximum and minimum sizes is cut out and prepared into special sands. The first method is followed when all the material from coarse to fine may be used in some grade of special sand for which there is a market. It is the simplest and most common method. The second method applies when a market exists only for grades between certain limiting sizes and

when the removal of some of these grades from the entire unsorted product will not damage, or may even improve, the grade of the remainder.

Drying.—Most special sands are shipped dry. For this reason it is simpler to dry the entire product in one operation and separate the dry sand, rather than to separate by wet screening and separately dry each size. Dry screening is more perfect than wet, especially for the finer grades, because surface tension of the water may cause a small amount of fines to adhere to the coarser grains and be carried over with the oversize.

Where glass sand is prepared, steam-heated driers are almost universally used. They are all of the type in which tiers of steam pipes form the bottom of the drier and support the wet sand. As fast as the sand dries, it falls between the pipes onto a conveyor that carries it to storage or the screening plant. This type of drier has the advantage of low maintenance and labor cost, it is fool-proof, there is no danger of discoloring or overheating the sand and it adds no fire risk to the plant. When discoloration is not objectionable rotary direct-heat driers burning coal, coke or fuel oil are used. Their thermal efficiency is probably higher than that of the steam driers, but they are a fire hazard, as overheated sand may set fire to elevator housings and bins. Coal-fired tower-type driers are used in some plants.

Screening.—Screening practice varies somewhat with the rigidity of specifications. If a graded product from coarse to fine may be used, as for some engine sand and stone-sawing sands, one pass through a revolving screen either wet or dry, after the silt has been removed by washing, is usually enough to remove oversize and foreign matter.

For close sizing between narrow limits all types of screens, sloping stationary, revolving and vibrating are used. Present practice, however, tends strongly to the vibrating type and practically all new plants are being equipped with them, even for the coarser sizes, 10-mesh to $\frac{1}{4}$ -in., whereas formerly they were only used for finer sizes, say below 10 mesh. If close sizing is necessary, the screens cannot be crowded to capacity. One company goes so far as to rescreen all its filter and sand blast grades.

Shipping.—Storage and shipping differs from that for ordinary sand as usually the material must be kept dry, which requires shipment in box cars. Some grades are shipped in less than car lots, especially filter, sand blast and standard sand. Shipments of less than a car load are made in paper or burlap bags.

USES AND PROPERTIES OF SPECIAL SANDS

The principal special sands and their characteristics or main specifications are as follows.

Filter Sand.—Filter sand is used especially for filtering municipal water supplies by mechanical or gravity filters. The sand must be

clean and free from clay, organic matter and flat particles. Not more than two per cent. should be soluble in hot dilute hydrochloric acid.

The terms "effective size" and "uniformity coefficient" are characteristic of filter-sand specifications. The effective size, expressed in millimeters, is such that 10 per cent. by weight of the sand is finer and 90 per cent. is coarser than the given size. The uniformity coefficient is the ratio of the size of grain (than which 60 per cent. of the sand is finer) to the effective size. Although rather an awkward way of expressing size and uniformity, it is almost universally used in filter-sand specifications. Effective sizes used vary from 0.20 to 0.70 mm. and uniformity coefficients from 1.25 to 1.80.

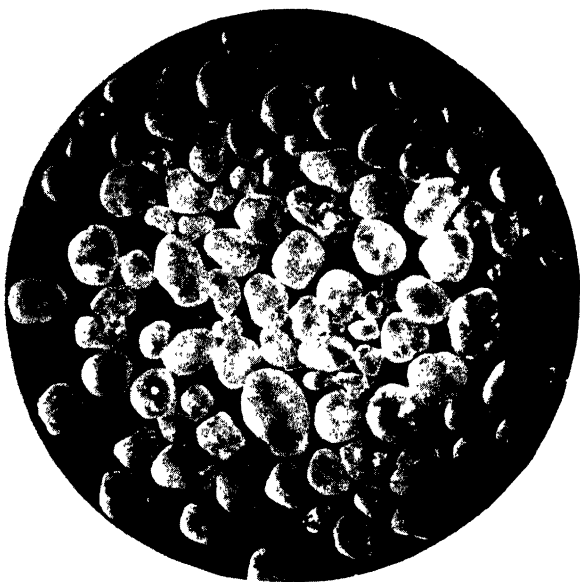


FIG. 1.—OTTAWA, ILL. FILTER SAND. $\times 10$.

Figs. 1 and 2, respectively, show a rounded-grain filter sand from Ottawa, Ill., and an angular-grained product from North Carolina.

Engine Sand.—Engine sand is used to prevent slipping of the driving wheels of locomotives of all kinds. It is very important and the total production is considerable. Unsuitable or poorly prepared sand is often used, but the better managed railroads are careful to select suitable material. It should be fairly uniform in size, free from large lumps or foreign matter that would choke the feed pipes, and free from clay, dust or other impurities that would tend to hold or absorb moisture and develop a natural bond. Engine sand is often shipped wet and dried at the supply or storage station. An ideal sand would all pass a No. 20

and be retained on a No. 80 sieve. One large railroad requires the sand to be 95 per cent. silica.

Fig. 3 shows a well graded and prepared engine sand and Fig. 4 a poorly prepared sand, dredged from the Potomac River and used as traction sand by the street cars of the District of Columbia and some railroads.

Abrasive Sands.—Abrasive sands include a large number of sands for special purposes. Some of them may require the most careful sizing and preparation, as sand-blast sands, whereas some may be ordinary unsized material such as is used for stone sawing. Usually, however,

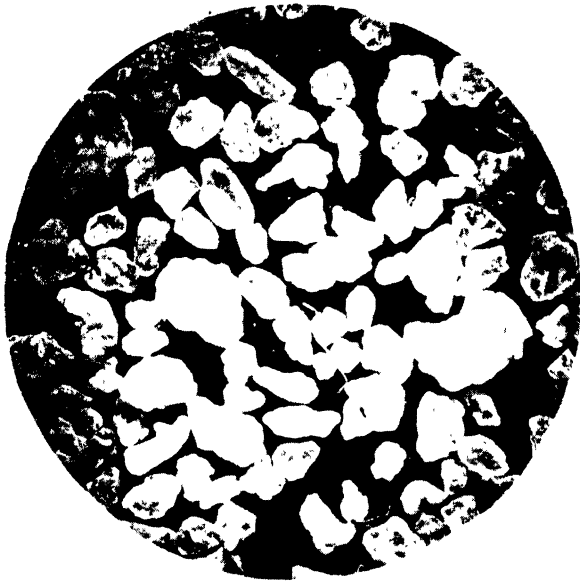


FIG. 2.—NORTH CAROLINA FILTER SAND. $\times 10$.

a graded or sized product is more efficient and is worth the extra cost if it does not have to be shipped too far.

Sand-blast sand is one of the most important of the group. It is prepared in different sizes from No. 1 to No. 4 to suit different classes of work. Some producers use trade names or some method of designating the different sizes, but they approximate roughly the above grading. Fig. 5 shows a very close-graded sand-blast sand from Ottawa, Ill.; Fig. 6, a No. 1 sand-blast sand prepared from New Jersey bank sand; Fig. 7, No. 1 sand-blast sand, also used as filter sand, prepared from a New Jersey ocean beach; and Fig. 8, No. 3 sand-blast sand prepared from bank sand near Millville, N. J. Considerable variations may be noted

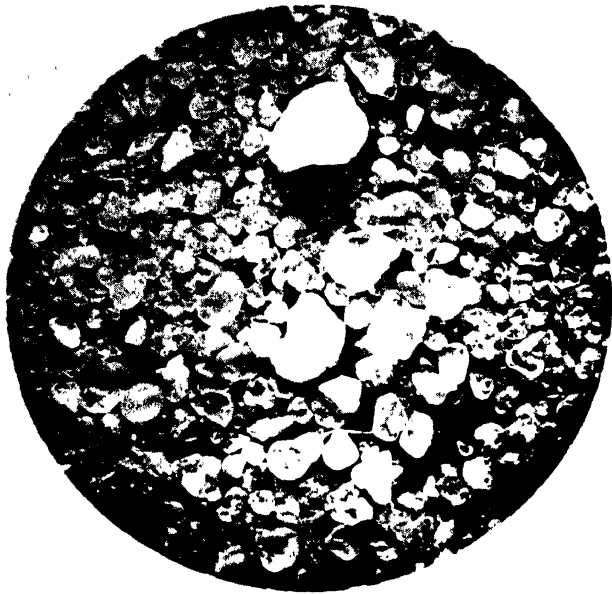


FIG. 3.—ENGINE SAND PREPARED FROM NEW JERSEY BANK SAND. $\times 10$.



FIG. 4.—ENGINE SAND PREPARED FROM POTOMAC RIVER SAND. $\times 10$.

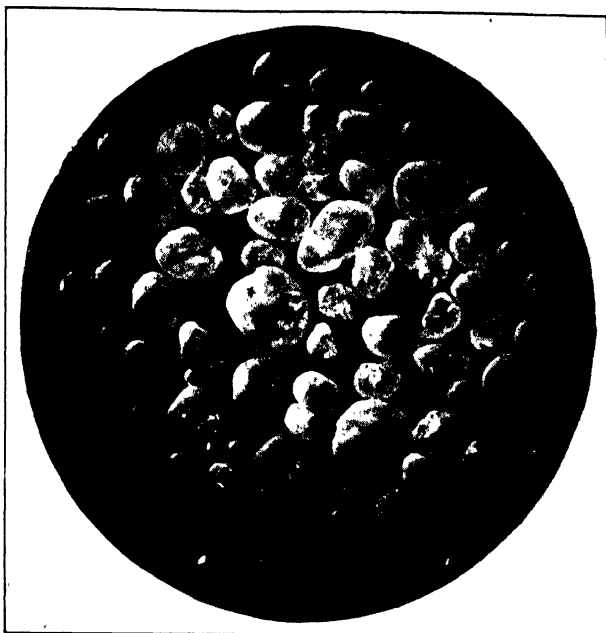


FIG. 5—SAND-BLAST SAND, OTTAWA, ILL. $\times 10$.

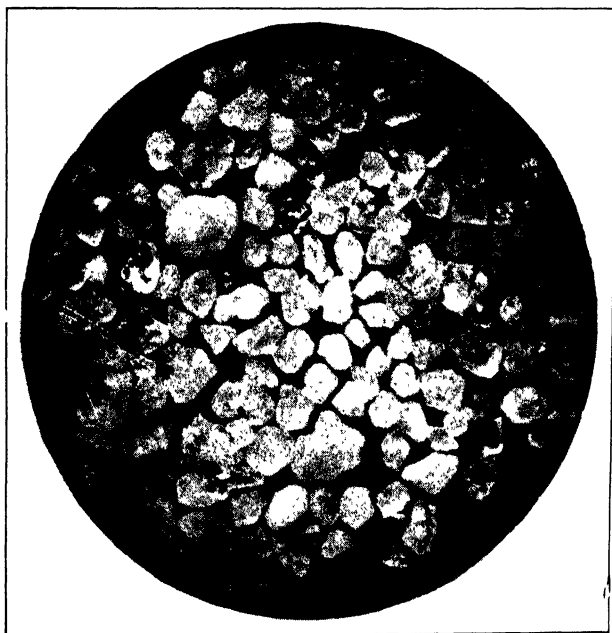


FIG. 6—No. 1. SAND-BLAST SAND PREPARED FROM NEW JERSEY BANK SAND. $\times 10$.

in the grades from different plants, but most of them range in size approximately as follows:

- No. 1, through 20 mesh and retained on 48 mesh;
- No. 2, through 10 mesh and retained on 28 mesh;
- No. 3, through 6 mesh and retained on 14 mesh;
- No. 4, through 4 mesh and retained on 8 mesh.

Sand for grinding stone, marble and plate glass and for similar uses is usually not a graded product. However, a washed sand with excess of fines removed and large particles screened out is desirable. Some



FIG. 7.—No. 1 SAND-BLAST SAND PREPARED FROM BEACH SAND. $\times 10$.

firms use the same sand for plate-glass grinding as for the melt. All of one such sand passed a 28-mesh sieve and 90 per cent. was retained on 150-mesh, being uniformly graded between these sizes. About 3 tons of sand are required to grind 1 ton of plate glass. Banding sand, a grade used for beveling glass, is finer than most grades and is often prepared by screening out the excess fines in glass sand or fine sand-blast sand. Usually it will have about 3 per cent. retained on a 35-mesh and 92 to 95 per cent. retained on 100-mesh screen. Sand for sawing and grinding stone is generally coarser than that used for glass. Some companies prefer to use a graded product about equal to No. 1 sand-blast sand, but most of it is not sized. One large marble company uses the sand shown in Fig. 9. It is a washed river sand with about 4 per cent. retained on a 10-mesh and 99 per cent. retained on 100-mesh sieve.

It should be noted that the photomicrographs shown are not intended to represent the relative amounts of coarse and fine grains, but rather the range from coarse to fine. Fig. 10 shows a washed bank sand from New Jersey, intended essentially for a core sand but suitable for most abrasive purposes. It all passes a 14-mesh and is retained on a 150-mesh sieve.

Formerly sand was used for coating sand paper. Very little is now used for that purpose as it has been displaced by crushed quartz, the more efficient artificial abrasives, or garnet.



FIG. 8.—NO. 3 SAND-BLAST SAND PREPARED FROM NEW JERSEY BANK SAND. $\times 10$.

Abrasive sands, in general, should be high in silica, which means a high-quartz content, clean and free from clay, and the grains should be tough and durable. There is some question as to the relative merit of rounded and sharp grains. Both are satisfactorily used and probably availability and price are more important than grain shape. Sharp grains are probably faster cutting at first, but rounded grains are more durable and do not break down so quickly. The color of abrasive sands is of no importance except as an indication of purity. There is, however, always a trade prejudice in favor of white sands.

Potters' Sand.—Potters' sand, which is also known as placing sand, is used by potters to place between the ware in the saggars, and, for heavy ware, between the ware in the kiln. Two grades, fine and coarse, are generally used. Both should be free from dust and fines and fairly well

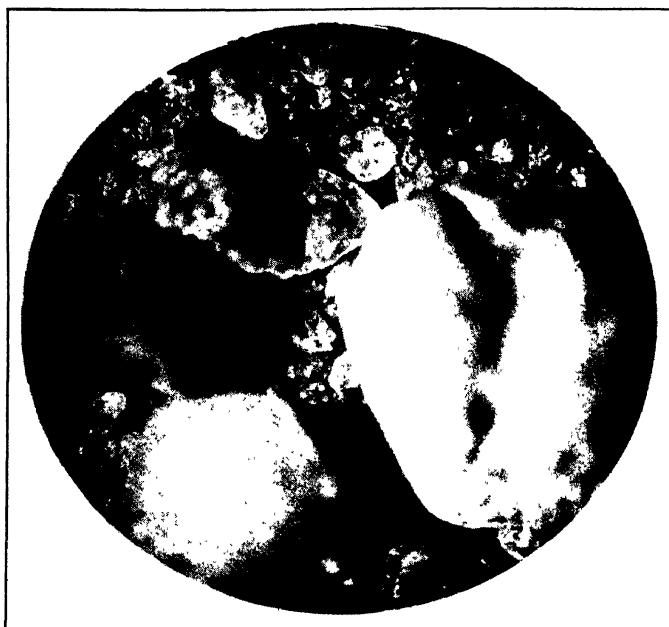


FIG. 9.—STONE-SAWING SAND FROM ALABAMA. $\times 10$.



FIG. 10.—WASHED BANK SAND FROM NEW JERSEY. $\times 10$.

sized. Material from 10 to 40 mesh is called coarse and 28 to 100 mesh, fine. Sand for white ware and refractories must be low in iron and fluxes. High purity is not essential for heavy dark ware.

Roofing Sand.—Roofing sand, as the term is here used, is employed as a coating on prepared rolled roofing. A sand white, or nearly so, is demanded and preferably a rounded-grain product. Manufacturers' requirements as to size vary somewhat, but generally a sand is required that will all pass 20 mesh with not more than 5 to 10 per cent. passing 100 mesh, which is about the physical requirements of a good glass sand.

Flooring Sand.—Flooring sand is the material used in asphalt mastic flooring that consists of asphalt cement, a sand aggregate and a fine mineral filler. The sand must be clean and free from clay and silt. It should all pass a No. 3 sieve, at least 40 per cent. should be retained on a No. 8 sieve, and not more than 8 per cent. should pass a No. 100 sieve.

Standard Sand.—Standard sand is a very uniformly sized product used in cement testing or as a standard with which to compare the effect of other sands in concrete mixtures. Only the rounded-grain St. Peter sand is used as produced at Ottawa, Ill., and after it has been carefully screened through a No. 20 and retained on a No. 30 standard sieve. The consumption is of course very small as it is for laboratory use only.

Sand for Oxychloride Cement or Plaster.—Sand for oxychloride cement or plaster is an important ingredient of this material. A white sand is preferable and it should be clean and free from clay and clay-coated grains. It must be decidedly finer than that used in Portland cement. Tests have shown that a good sand for this use will all pass a 10-mesh sieve, 95 to 98 per cent. will pass 20 mesh, and it should be well graded so that not more than 3 per cent. will pass 100 mesh. Both sharp and rounded-grain sand is used.

Sand for Chemical and Metallurgical Use.—Sand for chemical and metallurgical use is needed in the manufacture of sodium silicate and the artificial abrasive carborundum, or silicon carbide. For both these uses a sand that meets the requirements of a high-grade glass sand is acceptable. For sodium silicate, however, the iron and aluminum must be especially low as iron affects the color and alumina the solubility of the resulting glass. For silicon carbide, not more than traces of lime, phosphorus and magnesia must be present as they form unstable compounds. The sand should be free from dust, and in other physical properties it should equal a good glass sand.

Sand for Pulverizing.—Sand for pulverizing is used as a source of ground silica or quartz for use as paint filler, fine-grained abrasives, pottery, stucco, wall board and special plasters, foundry parting, soaps and similar uses. Only high-grade silica sands are suitable as both chemical purity and color are important. Regular run of prepared silica and glass sands are used and sometimes the fines screened out in the preparation of

coarser closely sized products, such as filter and sand-blast sands. Dust and fines are not objectionable unless they contain undesirable impurities. Iron oxide is objectionable and should be less than 0.05 per cent. Small amounts of alumina, lime and magnesia are not harmful. Oxides of other metals as titania are objectionable for the same reason as iron oxide, as they affect the color of the finished product in which the silica is used.

POSSIBLE BYPRODUCTS IN THE PREPARATION OF SAND

In the preparation of so cheap a commodity as sand, a possible recovery of valuable byproducts would hardly seem probable. Although this is true for most plants, it is believed that there are exceptions worthy of investigation. At some plants preparing a high-silica sand for various purposes, the wash water is settled and the fines marketed for special grades of molding sand, surfacing for tennis courts and sand for other uses. Also, it is believed, possible uses exist for the oversize screened out of some special sands, which are now thrown away as waste. In most plants, of course, whether the tonnage of such byproducts is sufficiently worth while is often a question.

At a plant in New Jersey preparing glass sand from a bank deposit, two grades of glass sand are prepared. The first, which is washed in the ordinary way, is suitable for common clear bottle-glass. For the best grades of crown glass for bottles, this washed sand is passed over James concentrating tables to remove the heavy minerals.

A partial analysis¹ of the washed sand, is as follows:

	PER CENT
Ferric oxide (Fe_2O_3)	0 07
Titanium dioxide (TiO_2)	0 129
Aluminum oxide ^a (Al_2O_3)	0 34

^a The Al_2O_3 contains any ZrO_2 that may be present.

A partial analysis of the washed sand after tabling is as follows:

	PER CENT.
Ferric oxide (Fe_2O_3)	0.03
Titanium dioxide (TiO_2)	0 032
Aluminum oxide ^a (Al_2O_3)	0 33

^a The Al_2O_3 contains any ZrO_2 that may be present.

The analysis of the concentrates, or material removed in tabling, is as follows:

	PER CENT
Silica (SiO_2)	7.7
Alumina (Al_2O_3)	4.0
Ferric oxide (Fe_2O_3)	24.2
Titanium dioxide (TiO_2)	52.8
Zirconium oxide (ZrO_2)	9 8

¹ All analyses were made by the U. S. Bureau of Mines.

With the ferric oxide content as a basis of calculation, 100 tons of sand would yield approximately 330 pounds of concentrates; using the titanium oxide content as a basis gives 367 pounds of concentrates; say an average of 350 pounds. A petrographic examination of the concentrate showed it to be made up of limonite, ilmenite, rutile, zircon, rock fragments and quartz. It is difficult to estimate the commercial value of this product as its value would depend on the ability to separate the different minerals into marketable products. This method of cleaning sand on tables might make possible the development of deposits not now workable. It is at least an interesting possibility.

POSSIBLE FIELDS FOR RESEARCH

Possible lines of research on special sands naturally group themselves under two heads: Preparation and utilization.

Preparation.—Under preparation there is ample room for study of efficient methods of washing, screening and drying. The best methods for these different processes have not yet been found for all conditions. The common practice is, of course, the usual procedure of adopting methods and equipment that have been used in the given district. Preparation studies would also include investigations of possible uses and methods of treatment of present waste products at sand plants, either as special sands or the waste products from the preparation of certain sands as mentioned under the tabling of glass sand in New Jersey.

Utilization.—Studies on the utilization of special sands would probably best be devoted to methods of testing physical properties for suitability for specific uses, with possibly some effort given to finding new uses. This latter, however, is believed to be of secondary importance. Specific problems that suggest themselves are, the relative advantage of sands of rounded and of angular grain for the different abrasive uses; a method of determining the toughness or durability of abrasive sands; a method of determining the abrasive value of sands; and relative advantages of a closely sized and unsorted sand for certain abrasive purposes.

A more rational method of defining the size and grading of filter sands ought to be devised, although the present method is very firmly established by usage among sanitary engineers. The sand producer, however, would welcome a more direct method. The relative advantages of better filtering of rounded-grained sand as compared with the greater surface area of angular-grained sand and the effect on the filtered water have never been definitely determined.

These and many other special problems make an interesting field for investigation. They cannot all be solved at once. Probably the accumulation of information from experience will decide most of them before they are solved by direct attack.

DISCUSSION

H. RIES, Ithaca, N. Y.—Blast sands are usually of a highly siliceous character. A former student now in Hawaii, attempted to clean some badly rusted iron work with volcanic sands of that locality, which are made of the fine sharp particles of lava. He was not very successful. Then he tried coral sand from the beach and found it worked better than the volcanic ash.

W. M. WEIGEL, Washington, D. C.—The difficulty with the volcanic sands was their low specific gravity. It would not have enough energy, velocity, or force to abrade the surface. Steel shot is, volume for volume, more efficient than sand, but the cost is one of the chief objections to it, and also the difficulty of keeping it from rusting.

Borate Deposits Near Kramer, California

BY HOYT STODDARD GALE, LOS ANGELES, CALIF.

(New York Meeting, February, 1926)

RECENT work on borate deposits near Kramer in the extreme southeast corner of Kern County, California, is of special interest because of the information it seems to give concerning the mode of origin of the borate minerals colemanite and ulexite, especially when considered in conjunction with the valuable clue to the mode of origin of colemanite in its present known deposits given in a paper by W. F. Foshag,¹ of the United States National Museum. Colemanite is found in or near original deposits of ulexite, from which it is supposed to have been derived by a change in the character of the ground water or rate of its movement or both.

Indications that an alteration of this sort had produced colemanite were first recognized by the writer² in specimens collected in the Kramer district in 1920, and sent to W. T. Schaller, at U. S. Geological Survey, for identification. The identity of the two borate minerals in these specimens was suspected when collected but not at once determined, but the relations of the minerals as seen in the specimens seemed to afford a manifest clue to the origin of the deposits. Similar specimens were obtained by the writer from deposits in Death Valley soon after he had examined the deposits near Kramer. After studying the specimens submitted to him Dr. Schaller wrote as follows:

"I have finally positively identified the boron minerals you sent me with your letter of Sept. 27. The 'white fibrous mineral like ulexite, is ulexite; the 'harder nodules' in the clay are colemanite, apparently formed from the ulexite as a result of leaching, with recrystallization in place—a theory that Foshag is working on."

The present paper is a report on the facts observed at the deposits near Kramer, and some general observations on the geological relations noted, which, unfortunately, still form only a very incomplete record.

The intimate association of deposits of colemanite and ulexite in California and Nevada with certain volcanic rocks affords a strong pre-

¹ W. F. Foshag: Origin of the Colemanite Deposits of California. *Economic Geology*, 16, (1921) April-May.

² Hoyt S. Gale: Origin of Colemanite Deposits. U. S. Geol. Surv. *Prof. Paper* 85 (1914), 3-9.

sumption in favor of the direct volcanic origin of the boric acid they contain. The occurrence of the larger deposits of borates in certain volcanic provinces, near lava flows that were probably particularly rich in boron, suggests their volcanic origin. It is well known that boric acid is emitted in solution from some volcanic vents, and these minerals are such as might have been formed by direct crystallization from solutions carrying boric acid or its immediate products. Perhaps the solutions containing the borate constituents were a part of the original magmatic waters. It therefore seems unnecessary to look farther for the original source of the boron in these deposits, at least until some facts are discovered that shall require a more complex explanation. Notwithstanding certain suggestions that have been made, there appears to be no direct connection between the nitrate and the borate salts that are found in some of the western deserts. If, then, we may accept the theory that these borate deposits are of immediate volcanic origin, we may find it possible to outline certain areas as primarily "borate provinces," within which deposits of borate minerals may be found, provided, of course, that other conditions are favorable to the occurrence of these minerals. The stratigraphic relationships of the known deposits of these borate minerals may afford the clue to some of the other favoring conditions referred to.

SPECIFIC EVIDENCE CONCERNING THE ORIGIN OF COLEMANITE IN THE KRAMER DISTRICT

The specimens first collected about the mouths of prospecting pits in the Kramer district (the shafts there were then inaccessible) were evidently nodules of mineral that had been formed in clay resembling the ordinary mud that is now being deposited in the intermittent lake beds of the desert basins. The nodules seem to have been entirely distinct and separate in the original clay matrix, and most of those first seen were smaller than a man's fist.

Some of the nodules, when broken, were seen to be composed of a hard, radially-crystalline mineral, which was made slightly gray by included mud but would presumably have been white or glassy clear if pure. Other nodules were composed of a milk-white silky-fibrous, almost chalky mineral, in which the fibers are crinkled or irregularly wavy. This silky fiber suggested the mineral ulexite, but it seemed harder than the ulexite found in the moist surface clay about the margins of playa lake beds. The appearance of some of the broken nodules indicated that the mineral ulexite, of which the nodules were originally composed, had later been in part recrystallized within the nodules to form a secondary mineral, which proved to be typical colemanite.

Significance of Kramer Deposit Specimens

The special significance of the specimens obtained from the deposits near Kramer lies in the fact that the borate minerals are scattered through the clay or shale as separate nodules, essentially in the way in which they seem to have been first formed within the enclosing mud. Almost all other colemanite deposits visited by the writer seemed to have undergone greater alteration from some original form, partly by mechanical breaking due to shattering, crumpling, and dislocation of the enclosing beds and partly by the recrystallization of the colemanite in secondary veins along fractures made across bedding or other structural planes. The Kramer deposits seem exceptional in that they show the simplest mode of formation of these minerals yet noted. Many of the other well-known deposits of colemanite consist of great irregular, broken masses, in which the pure crystalline mineral is mixed with squeezed clay or shale and fragments of detritus of other rocks in a manner that obscures the determination of their origin.

In his former paper the writer regarded colemanite as a vein deposit, using the term "vein" to cover also deposits formed by metasomatic replacement, the present ore mineral having been produced from another different mineral by chemical processes and deposited within a certain ore zone in the enclosing beds. This explanation was contrasted with the former suggestion of the mode of origin of these minerals, namely by precipitation as a "saline residue" from solution by the evaporation of surface waters—such a residue, for example as the common salt and soda found in the beds of western desert lakes. Natural borax does form by evaporation of saline waters, and for a long time deposits of colemanite and ulexite were included in the same class as deposits of borax.

The writer takes this opportunity to revise in one particular the views he tentatively expressed in his former paper on the origin of colemanite, and he considers himself fortunate in finding so good an example showing the origin of this mineral. In his former paper he suggested that colemanite might have been formed as a replacement of limestone, in which carbonic acid might have been replaced by boric acid derived from percolating ground-water solutions derived from volcanic rocks. This reaction is not probable under ordinary conditions—a fact that was recognized when the suggestion was made—but certain observed intergrowths of colemanite and limestone seemed to suggest that the reaction had really taken place. Specimens showing the intergrowths referred to are probably still in the collections at the U. S. Geological Survey or the National Museum, and possibly also at the Massachusetts Institute of Technology, to which one sample was sent for inspection by Dr. Waldemar Lindgren. However, this one postulate in the original hypothesis

of the writer was very far from finally determined, and the facts now available furnish a much more general and satisfactory explanation of the origin of most of the known large deposits of colemanite.

Origin of Colemanite Deposits

The most plausible explanation of the origin of deposits of colemanite is that which has lately been developed by Foshag, who writes as follows:

"Ulexite is the common borate occurring in the playa lakes, where it is found with borax and salt . . . By leaching ulexite with sodium chloride solutions instead of pure water he (Van't Hoff) obtained colemanite. The reaction is completely reversible and, by varying the amounts of borax, can go in either direction—colemanite and borax may result from ulexite or ulexite from colemanite and borax. If an excess of borax is present, any colemanite is converted into ulexite; while if the borax is removed as it is formed the ulexite will break down completely, giving colemanite if the solution is salt-bearing."

Ulexite is a common mineral in the muds of many playa lakes in desert regions, especially in certain volcanic districts. Deposits of ulexite originating in a way similar to that of the more modern deposits were formed in early geologic time. Most of the colemanite deposits that we now know in California and Nevada are in beds of Miocene age. Ulexite of the well-known playa type of deposit is usually found around intermittent desert lakes, and Foshag contends that its deposition was made possible by the presence of an excess of borax in the ground water and that the ulexite therefore remained for a time fairly permanent. "When these deposits were later covered over and uplifted sufficiently to allow free drainage from the beds, the percolation of sodium chloride solutions gradually converted the ulexite to colemanite."

The evidence afforded by the deposits themselves seems to support this or some closely related theory of origin. Some of the specimens collected from beds about Kramer show ulexite and colemanite intergrown in the same nodule, as if the colemanite had been formed by only the partial recrystallization of an original ulexite nodule. The presence of masses of solid ulexite in some parts of this district and only colemanite nodules in others would seem to indicate that the conditions leading to one or the other mode of formation were very nearly balanced. Thus the reaction producing colemanite in this district is apparently not complete, and perhaps we see here evidence of the transition in process. Not much of the colemanite formed seems to have been carried away from the nodules containing the original borate mineral, and the fact that the colemanite was not crystallized into secondary veinlets here, as it is at many other places, indicates that the influences which effected the transformation were not very active at this place.

HISTORY OF DISCOVERY OF BORATE MINERALS AT KRAMER

The announcement of a new "borax find" appeared in California newspapers under large headlines in October, 1913. At first the discovery was credited to F. M. Smith ("Borax Smith"), but later it appeared that Mr. Smith took little, if any, part in it.

Dr. John K. Suckow, a physician of Los Angeles, had made a desert-land entry on the northwest quarter of Sec. 22, T. 11 N., R. 8 W., and in boring a well for water near the middle of this tract encountered deposits of a crystalline mineral that attracted enough interest to justify a test, which proved it to be a borate. Testimony given in court under oath shows that these deposits were found at depths ranging from 369 to 410 ft.

The well that penetrated these deposits was bored on the broad, sloping, sage-covered plains on the northern border of the Mojave Desert, in a district that is sparsely settled. This district is in the corner of Kern County, about 10 miles northwest of Kramer, which is in San Bernardino County, and about 25 miles directly east of the town of Mojave. The deposits themselves are only about four miles north of a small station called Rich, on a main line of the Santa Fe R. R., with which they are now connected by a rather sandy stretch of direct and almost level road. The transportation facilities are thus exceptionally good as compared with those in most other districts that contain commercial deposits of borate.

The agricultural entries on lands in this district were apparently relinquished soon after colemanite had been found on them, and other entries were then made as mining claims, mostly in placer form, on these and adjacent public lands, of which alternate odd-numbered sections already belonged to the Southern Pacific R. R. by virtue of the original grant made from the public lands. Soon after the discovery became known, not only the Suckow property but several other holdings in this district passed into the control of the Pacific Coast Borax Co., either in its own name or in the name of allied organizations, such as the United States Borax Co. and the Borax Consolidated, Ltd., the latter being the parent organization in London. This company now owns most of the known borate-bearing land in the district, the most conspicuous exception being a certain tract that is in part withheld by Dr. Suckow, on which he has now developed commercial production and from which he is manufacturing borax at his plant in Los Angeles.³ Shafts recently put down by Dr. Suckow on his own initiative have led to a revival of interest in the commercial possibilities of this district.

³ Since this paper was written, the original Suckow holdings, including the Suckow interest in the borax manufacturing plant at Los Angeles, have been sold to the Pacific Coast Borax Co. Dr. Suckow still claims an interest in certain lands outside of the original holdings, but his claim has been a subject of litigation. (Dec., 1925.)

It is unfortunate that much of the geologic evidence concerning such deposits as this, and in fact concerning most of the borate deposits mined in this country and abroad, is rendered unavailable to the public by the policy of secrecy maintained by nearly all those who are interested in them. The borax industry has been essentially monopolistic, and the monopoly has been maintained by policies in which secrecy seems to be essential. Now, however, a new source has entered the field successfully—namely, the saline deposits at Searles Lake—and so long as these enterprises remain independent of the company that now holds almost all other potential producing borate deposits in the world we may consider the production of borax a competitive industry.

EXPLORATION AND DEVELOPMENT IN THE DISTRICT

The desert north of Rich station, on the Santa Fe R. R., consists of a broad, gently sloping plain, covered with sagebrush and having a very sandy or gravelly soil. This plain rises from an elevation of about 2350 ft. at Rich station to one of about 2500 ft. at the foot of the mountains that form its northern border. This plain is part of a great stretch of alluvial waste over which intermittent drainageways have poured rock detritus over broad, flat, merging slopes, converging toward low points in the desert, and forming equally intermittent water-bodies, whose flat basins, when dry, are known as "playas" or dry lakes.

Near Rich the surface deposit of the plain consists largely of granitic materials, such as quartz sand, gravel, and more or less broken boulders, with which are mixed fragments of basaltic lava and chalcedony derived from nearby volcanic rocks. In the vicinity of the borate prospects this surface wash forms a deposit about 100 ft. thick, which the miners call the "overburden." The water in this region is usually found in this surface deposit, although at some places small supplies are obtained from the underlying strata. This alluvial cover masks all signs of the underlying rocks, which are revealed only at places where the hills bordering the plains rise out of the alluvium. The rocks exposed at such places consist of hard lavas, which occur as flows interbedded with the sediments, and of intrusive masses. Large areas of granite occur in the higher hills to the north.

A section that is characteristic of the beds encountered in prospecting in this region consists of the following members:

1. Gravel and boulder overburden at the top.
2. Clay or mud, described by the miners as "green shale," with some sandy layers and here and there arkosic sandstone and conglomerate. This formation overlies the borate-bearing beds, and is not reported to contain borates.
3. Clay of gouge type, generally dark bluish-green or gray, locally called "blue shale," through which the borate minerals are scattered in

nodules. This clay is usually moist when first removed from the ground, and its moisture gives it a darker color than it would otherwise have.

4. Basaltic lava, much of it vesicular; evidently flows interbedded with the sediments.

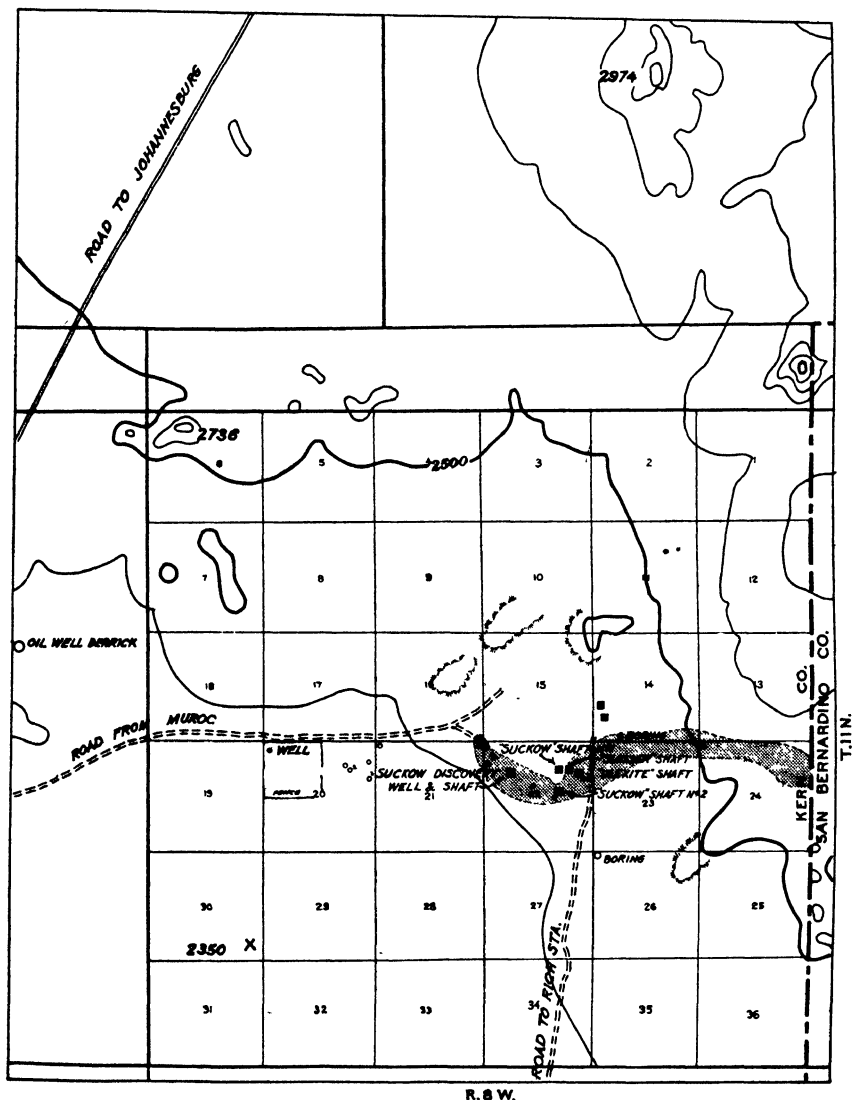


FIG. 1.—MAP OF KRAMER BORATE DEPOSITS NEAR RICH STATION, CALIFORNIA.

The accompanying map of the Kramer district, showing the location of the principal prospects that have been sunk for the borate minerals, is based upon a contoured topographic map published by the U. S. Geological Survey—the Searles Lake sheet.

For some time the only evidence available concerning these deposits was that reported for the original discovery. A partial log of the Suckow discovery well in Sec. 22, obtained from testimony given in a certain court case is as follows:

DEPTH IN FEET	MATERIAL
190-331	Clay, dark, putty-like
331-369	Shale, blue
369-410	Colemanite
410-435	Shale, blue
435-445	Gypsum
445-450	Rock formation

The beds here described as gypsum may consist of some other material for no gypsum has been found in other parts of this deposit. The rock formation at the bottom of the boring is probably the basaltic lava referred to elsewhere. A shaft was sunk later at the site of this well, but as it was carried down only about 200 ft. it reached only the so-called green shale and probably did not encounter any borate minerals. On the dump at this shaft are specimens of dry, dark greenish-gray clay, which was perhaps originally shale.

The prospecting that led to the discovery at Kramer was followed by other prospecting, chiefly by the borax company, of which the following incomplete records are available. A shaft near the middle of the north-east quarter of Sec. 22, known as the Slosser shaft, encountered nodular borate minerals in a bed 10 to 14 ft. thick at a depth of 110 ft., and this bed was immediately underlain by a mass of vesicular basaltic lava, which was excavated to a further depth of several feet without reaching its bottom. Ore taken from this working stood in sacks at the mouth of the pit, exhibiting specimens of ulexite and colemanite like those here considered.

The Ulexite Shaft

Another shaft, about 600 ft. S. 70° E. of the Slosser shaft, has been called the Ulexite shaft, because a quantity of the hard form of the milky-white silky-fibered ulexite was found at this place. Ulexite is reported to have been encountered also at a depth of 110 ft., and the boring was sunk only about 10 ft. deeper, into a solid-looking body of this mineral. Evidently considerable pains have since been taken to conceal whatever was found at this shaft, as the entrance was blocked and access was denied, but excellent specimens of ulexite were seen on the dump. A boring some 40 ft. south of this Ulexite shaft also brought up ulexite, and reached the top of the basalt sheet at a depth of 190 ft. These workings are all in Sec. 22.

Other borings were put down at about the same time the work just described was being done. A boring near the south boundary of Sec.

14 is reported to have encountered borates at a depth of 275 ft. Several other shallower shafts and borings northwest of the center of Sec. 14 yielded results not definitely known to the writer.

A boring sunk by John L. Hannam and associates in the northwest corner of Sec. 24 is reported to have struck borate minerals in quantity at a depth of 250 ft. The claim was afterward bought by the borax company. Other prospecting in the northeast quarter of Sec. 24 is said to have found some of the most promising ground in the district, but this land also has passed into the control of the borax company, and details concerning it are not available. W. Scott Russell drilled a hole in the extreme northeast corner of Sec. 21, encountering light greenish shale at a depth of about 120 ft. and finding a good showing of colemanite at 160 to 180 ft. Another hole was started in the southeast corner of Sec. 16, but the property so prospected was sold to the borax company before the boring had reached a sufficient depth for an adequate test, and the work was stopped. Another hole was put down by the borax company in the northwest corner of Sec. 22 to a reported depth of 260 ft., but the result is unknown to the writer. Another boring near the middle of the north half of Sec. 22 (depth reported, 250 ft.) and one near the middle of the same section encountered some borate minerals, but no details concerning them are available.

Three prospect wells have been drilled recently in the northeast quarter of Sec. 20 by Geo. M. Kohler, evidently in search of a possible western extension of the borate belt. These test wells were all unsuccessful. Basaltic lava was encountered in each well; in No. 1 at a depth of 269 ft., in No. 2 (just southeast of No. 1) at 207 ft., and in No. 3, which was drilled near the center of the east edge of the section, at 240 ft. Green shale was struck below the usual 150 ft. of gravel overburden, and deeper a thin showing of blue shale, but the latter yielded no borates. Another well, drilled by others still later, about 1000 ft. north of the No. 3 Kohler well, encountered green shale at a depth of 120 ft., a small bed described as blue shale at 195 ft., and basalt at 250 ft., but no borates.

Suckow Shaft No. 2

Work of special interest was done in the summer and fall of 1924 by Dr. Suckow. A shaft was sunk near the middle of the northeast quarter of Sec. 22 on property then partly in Dr. Suckow's control and close to a similar shaft put down by the borax company. The result of the borax company's work was evidently not known to Dr. Suckow at the time, for he began to sink a mining shaft that reached basaltic lava at a depth of 180 ft. but found no borate minerals. Apparently in spite of some opposition, and with persistence characteristic of the prospector, Dr. Suckow then continued his work at a place near the middle of the south

side of the northeast quarter of Sec. 22, about 1000 ft. south of his unsuccessful shaft, where, by drilling a series of preliminary borings, he discovered a considerable body of borate minerals. He then began to sink a regular mining shaft, with results described as follows:

LOG OF SUCKOW SHAFT No. 2, SEC. 22, T. 11 N., R. & W.	
DEPTH (FEET)	CHARACTER OF MATERIALS
0	Sand and gravel at mouth of shaft, at an elevation of about 2400 ft.
0-105	"Overburden," alluvial wash consisting of sand, gravel, and boulders of granite and basalt.
105-170	Shale, described as green, with a caliche-like lime at its contact with the overlying beds.
170-210	Sandstone, arkosic, and conglomerate made of fresh to partly disintegrated granite, this being a distinctly interbedded part of the borate-bearing series.
210-280	Shale, moist, dark-greenish when fresh, through which lenses or nodules of borate minerals were irregularly scattered.
280-330	Basalt, massive, compact, evidently a part of an interbedded volcanic flow.

The contact of the arkosic sandstone with the underlying borate-bearing shale showed apparent stratigraphic conformity, and the beds appeared to strike N. 70° W. and to have a southerly dip of about 25 deg. Near the bottom of the shaft, at a depth of 330 ft., at the contact of the borate-bearing shale with the underlying basalt, the beds seemed to strike about N. 40° W. and to have a southerly dip of 50 deg. As seen in the shaft the borate-bearing shales are so greatly contorted as to show much variation in structure, and it would be difficult to determine their general trend from the small space that was open for observation at the time of the writer's visit.

A boring put down 100 ft. southwest of the site of the present mining shaft gave the following log:

DEPTH IN FEET	MATERIALS
0-105	Gravel and granitic wash debris, alluvial.
105-180	Clay or shale without definite showing of borate minerals.
180-275	(Not reported.)
275-280	Shale, blue.
280-282	Shale, giving test for borates.
282-289	Colemanite.
289-297	Colemanite nodules in clay.
297-300	Colemanite.
300-301	Shale, blue.
301-303	Colemanite and ulexite.
303-305	Colemanite.
305-314	Colemanite nodules in mud.
314-329	Colemanite.
329-339	Colemanite nodules.
339-351	Shale, blue, containing nodules of colemanite.

The subsequent development on this ore body in the mine seems to indicate that such a record as the above—an interpretation of well-cuttings and drillers' notes—is very unsatisfactory, because the driller usually places too much emphasis on the more noticeable economic features of his work, as, for example, the crushing of the harder nodules of colemanite, although the deposit is composed predominately of clay. In the mine this section was found to consist largely of clay or shale containing nodular masses, up to a foot or more in larger dimension and consisting of more or less compact colemanite, at many places rather intimately mixed with the clay.

The ore zone developed by this work has the appearance of a fault gouge. Where the enclosing strata are less contorted the colemanite lies in lumps that conform essentially with the original bedding of the clay. No secondary recrystallization of the colemanite in the fractures was noted. It is still uncertain whether there has been extensive faulting between the borate-bearing clays and the basalt or whether the contortion observed is merely the result of crumpling of the soft shale or clay against the rigid mass of the basalt. The writer is inclined to favor the latter alternative, although in the mine the basalt seems shattered through a considerable zone underneath the gouge-like clay containing the borates.

The deposit of colemanite here is not nearly so large nor so free from included clay, etc., as many deposits that have been mined commercially elsewhere. The record of Dr. Suckow's present work, however, is very encouraging. The larger blocks of colemanite, which were being sorted as the material was hoisted from the mine, were furnishing daily about six tons of shipping ore that was said to yield an average of 32 to 35 per cent. of anhydrous boric acid, without calcining or other separation or purification. After this ore has been roasted and ground its average content of acid is increased to about 40 per cent. The material is said to be readily adapted to the ordinary methods of treatment employed for converting colemanite to borax, and the output here has been regularly utilized in this way at the refining plant in Los Angeles. Although at the time of the writer's visit a considerable part of the cost of operation would be properly chargeable to development and standardization of methods, it was understood that the product was being obtained as raw material for the Los Angeles plant at a total cost not much different from that of colemanite mined elsewhere. As the work on the Kramer deposits proceeds the product can doubtless be obtained and shipped in a much more efficient way than it is at present.

The review of the foregoing details, aside from their stratigraphic significance, is considered justified by the need of putting the facts on record for such practical use as they may prove to be in determining the further commercial resources of the district.

STRATIGRAPHIC RELATIONS OF THE BEDS CONTAINING THE BORATES

The exact geologic age and stratigraphic position of the borate-bearing series is still in some doubt, but evidence accumulating from various sources indicates that most of the known deposits of colemanite are of approximately middle Miocene age. Although the stratigraphy of the marine series on the west side of the Coast Ranges and in San Joaquin Valley has been well worked out and the determinations of their age are supported by rather abundant paleontologic evidence, the correlations across the ranges from these marine sections over into the Mojave Desert region and farther east are obscure, and fossils are not abundant in the desert. This problem deserves careful study, and the writer will not here attempt to present a thorough review of the evidence available.

The borate deposits occur in a series that has been called the Esmeralda by King in his reports on surveys made along the 40th parallel and in later reports; the Siebert Lake beds by Spurr and others in reports on Nevada geology; and the Rosamond series in reports on the Mojave Desert region of California. Later the terms Ricardo series and Barstow series have been applied to rocks of about the same age in the Mojave region. The Barstow series probably includes the borate-bearing beds near Daggett and elsewhere, which are considered late to middle Miocene. The Ricardo series is considerably younger than the Barstow; it is supposed to be of latest Pliocene age. The type Rosamond may overlap the Barstow, although Buwalda⁴ suspects this Rosamond is older even than the Barstow. The Rosamond consists largely of volcanic rocks and is not so typically a desert formation as either the Ricardo or the Barstow.

Perhaps the most direct tie between the marine Tertiary deposits of the Coast Ranges of Southern California and the inland lake deposits of the desert region may be found in the series of volcanic flows that lie along both sides of the Tehachapi Mountains. The deposits of colemanite in northeastern Ventura County are associated with a series of basaltic flows that is probably contemporaneous with a series of like flows at the southern edge of the San Joaquin Valley—a series that is pretty well defined in age by its marine fauna. Pack,⁵ in describing the Tertiary volcanic rocks of the oil-field district in southern California, suggests their correlation with the Tertiary volcanic rocks of the borate district in the Lockwood Valley, just across the San Emigdio Mountains. Flows of basalt and sills of the same kind of rock occur in the uppermost part of the Vaqueros formation and in the overlying diatomaceous Maricopa shale. An older series of volcanic flows, consisting of tuff, andesitic agglomerate, and scoriaceous basalt, lies in the upper part of

⁴ Personal communication.

⁵ R. W. Pack: The Sunset-Midway Oil Field, California. U. S. Geol. Surv. *Prof. Paper* 116, (1920) 52.

the Vaqueros formation and is far more widespread than the younger series of flows referred to above. These lava flows were probably laid down in part beneath marine waters and in part subaerially. The Vaqueros formation is assigned to early Miocene time, and the diatomaceous Maricopa shale, often referred to as Monterey shale, abundant in the southern Coast Ranges of California, may be regarded as of middle to late Miocene age. The writer now believes that the borate deposits are associated with some of the later or younger rocks referred to above.⁶

Longwell, working in southern Nevada,⁷ places the borate-bearing beds of that region in his Horse Spring formation, and suggests the correlation of that formation with the Siebert and Esmeralda formations of southwestern Nevada, because of agreement in lithology and degree of deformation, as well as in general regional relations. He decides that these beds are of upper Miocene age.

"BORAX" MINING CLAIMS

There is no reason to doubt that the colemanite deposits that are commercially worked today are lode deposits within the original meaning and intent of the United States mining law. Colemanite claims have been patented for both lodes and placers, so that precedents have been established for both forms. However, this practice has undoubtedly been followed because those who are entrusted with the administration of the mining laws have been uncertain as to the true geological character of a colemanite deposit, and they have undoubtedly acted upon the best information available to them at the time the decisions were made. Not only the land officials, but even those who have worked upon the deposits themselves have been uncertain as to the form and origin of the deposits. As a consequence lode and placer claims and patents in the same mining districts are maintained on essentially the same deposits, although the maintenance of a claim on one form is in itself a contradiction of the claim in the other.

This contradiction has been of somewhat natural development. Borax is a water-soluble mineral, and it is found in the evaporation deposits of some of the desert lake basins. It is deposited there by the evaporation of saline solutions, just as many other salt deposits have been formed. The United States mining law, by a special act, has recognized salt deposits as locatable and patentable by means of placer claims. Therefore, it has been natural to assume that a mineral salt like borax might be included in the same class with common salt. But the natural deposits of borax found in some of the desert salt marshes are

⁶ Hoyt S. Gale: Borate deposits in Ventura County, California. U. S. Geol. Surv. Bull. 540, (1914), 434.

⁷ C. R. Longwell: Geology of the Muddy Mountains, Nevada. *Am. Jour. Sci.* 50, (1921), 52.

distinctly different from the deposits of ulexite or the colemanite from which artificial borax is now chiefly manufactured. All of these minerals may occur in the same mining district.

Many of the earliest workings of borate minerals were located on the so-called cottonball or ulexite deposits. When these were located as mining claims there was some reason for the general assumption that the placer form of location should apply to them also. There was no specific authority in mining law for classifying them as placer deposits, but apparently such a classification was generally adopted by those in charge of the administration of the mining laws. It is true that the mineral ulexite originates in stratified or bedded deposits, as in the muds laid down about the borders of intermittent lakes, and so, being imbedded in more or less horizontal deposits of water-distributed sediments, they may have seemed in this regard analogous to true placer deposits, such as those of gold in stream gravels and sands. There is, however, an essential difference, for ulexite is not itself a reworked and water-transported mineral; it is a mineral that has crystallized within the mud in which it is now found, into which it was introduced by a process similar to common processes of vein mineralization, the constituents of the mineral having been derived by chemical reaction of constituents from percolating ground solutions. Thus the ulexite deposits that are found in the saline playas of the deserts are not placers in a geological sense, and it seems that they have not been specifically defined as such by any provision in the United States mining laws. Probably it remains for the courts to decide whether such deposits have ever properly been classed as placers.

The Case of Colemanite

Colemanite, however, presents an even clearer case than the ulexite or cotton-ball deposits, for it is in no sense a placer deposit, nor does there seem to be any specific authority in the United States mining law for considering it such in a legal sense. Even if this mineral had been originally laid down in true bedded form in sedimentary deposits of sand, clay, or other material, it would still not be a placer deposit in the geological sense, any more than are deposits of coal or phosphate or many other normally interbedded stratified deposits. The proper classification of the bedded phosphate deposits of Idaho, Utah, and Wyoming was the subject of a long drawn-out legal controversy, and the decision concerning them would apply equally to the colemanite and ulexite deposits. The Department of Interior has decided that the western phosphate deposits are subject to location as lodes and not as placers, and this decision was reached after mature consideration of the contentions of locators having claims in both forms. Perhaps a corresponding official decision with regard to borate deposits cannot be satisfactorily reached

until an actual case is presented either to the Department of Interior or to the courts and the matter is officially reviewed, or until some act of Congress similar to that applicable to phosphates shall be passed to cover borates.

The legal aspect of the question is considered here primarily to call attention to the fact that colemanite is not, in fact, a detrital sedimentary deposit, but is in every sense a *lode* as defined by the original mining laws, because the mineral has been formed by the alteration of another original borate mineral, which itself was introduced by chemical or mineralizing processes into beds that had first been laid down by sedimentary accumulation. Colemanite cannot be considered a product of desiccation—that is, a residual crystallization obtained by the evaporation of pre-existing lake waters—even if that view would afford justification of the contention that it occurs in placers. Colemanite is undoubtedly a vein mineral of the metasomatic replacement type, and it should never have been regarded as other than a lode deposit within the meaning of the mining laws.

Mechanical Properties of the Aluminum-Copper-Silicon Alloy as Sand Cast and as Heat Treated

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(Syracuse Meeting, October, 1925)

In this paper are given the mechanical properties, determined by the Engineering Division, Air Service, U. S. A., of the 94 per cent. aluminum, 5 per cent. copper, 1 per cent. silicon alloy as sand-cast and as heat-treated commercially to Air Service Specification No. 11,300. This particular alloy was tested both in the cast and in the heat-treated condition. Tension and tension modulus values were obtained from machined and from un-machined test specimens; while data for shear, compression, impact, torsion, and for Brinell and Rockwell hardness were found from machined bars. Specific-gravity tests were made on sanded, un-machined specimens. The metallography of the alloy is useful as a control to heat treatment and presents some interesting peculiarities in regard to the two iron-bearing compounds.

THE demand for an aluminum alloy, suitable for sand castings, that may be heat treated to meet requirements of high strength, ductility, shock and corrosion resistance, and ready machineability has led to the commercial development of a proprietary material that contains from about 4 to 5 per cent. of copper, 1 per cent. of silicon, and such impurities as iron, up to a maximum of 0.75 per cent., and manganese, in quantity usually less than 0.1 per cent.¹ Magnesium is not generally present, for it tends to nullify the beneficial influence of the added silicon by forming magnesium silicide. The function of the silicon is to minimize casting difficulties and, structurally, to favor the precipitation of (insoluble) iron-bearing skeletons rather than the needles, which prevent full realization of tensile properties from heat treatment by stimulating intergranular fracture. The amount of silicon necessary to counteract the ill effect of iron is equal to or slightly more than the content of iron; the excess of silicon over this ratio, under certain conditions of heat treatment, enters with CuAl_2 , the principal hardening constituent, into solid solution and contributes somewhat to the strength of the alloy without appreciably impairing its ductility.

The schedule of heat treatment of this alloy depends on the design (cross-sections) of the castings and on the nature of the tensile properties desired. Essentially, the process consists in heating the material at about 950° F., quenching in oil or in cold or boiling water, and artificially aging

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¹ See U. S. Patents 1472738 (Oct. 30, 1923) and 1508556 (Sept. 16, 1924).

at temperatures of from 212° to 300° F. for approximately 2 hr. The soaking period at 950° F. is on the order of 24 hr. or longer; this solution treatment is much more protracted than that for chill-cast or worked alloys because of the initially larger size of the soluble compounds.

The importance of the aluminum-copper-silicon alloy and others of its type as a material for engineering purposes deserves a prominence that is bound to be enhanced as time passes. The cost of heat treatment is a considerable factor; but this may be overshadowed by the mechanical and physical characteristics as referred to the specific gravity, which is about 2.79. Such cast and heat-treated aluminum alloys may, therefore, in many cases be competitors of the heavier steels, brasses, and bronzes. In aircraft construction, for instance, the former have been used for pump and fuel-system parts, brackets, levers, wheels, cylinder blocks, crankcases, supercharger casings, and a variety of smaller castings.

The present paper describes the properties of the 94 Al-5 Cu-1 Si alloy as obtained by the Material Section, Engineering Division, Air Service, U. S. A., at McCook Field, Dayton, Ohio, from commercially sand-cast and heat-treated test specimens, gated according to two methods—that of the Air Service, and that of a manufacturer.

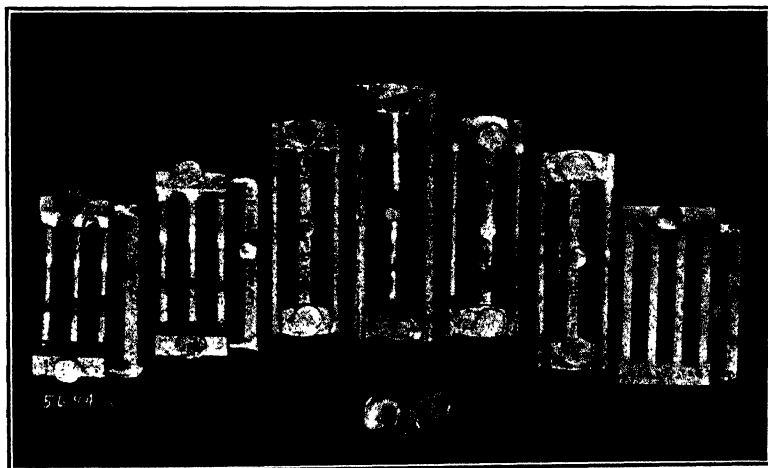


FIG. 1.—METHOD OF GATING USED BY MANUFACTURER.

MATERIAL

The aluminum-copper-silicon alloy was supplied in the form of test specimens in three heats—melts 3552, 3551, and 3686. In order to facilitate the stamping of the test bars, these melts were designated as C, HT, and Z, respectively, C representing material as sand-cast and HT and Z as heat-treated. The test specimens from melts C and HT were gated by the manufacturer according to his methods (Fig. 1); those from melt Z according to Air Service methods (Fig. 2).

Seven types of standard Air Service test specimens were cast as follows:

TYPE SPECIMEN	KIND OF TEST	NUMBER BARS TO MOLD
TB1	Tension, not machined	3
TB1A	Tension, machined	3
TB4	Shear, machined	2
TB4	Compression, machined	2
TB6	Impact, machined	4
TB7	Torsion, machined	2
TB13	Tension modulus, not machined	2
TB14	Tension modulus, machined	2

The analyses of the three melts follows:

MELT	DESIGNATION	COP- PER, PER CENT	SILI- CON, PER CENT.	IRON, PER CENT	MAGNE- SIUM, PER CENT.	MANGAN- ESE, PER CENT.	CHROM- IUM, PER CENT.
3552	C	4 90	0.80	0.62	Tr	0.04	Nil
3551	HT	4 93	0.84	0.62	Tr	0.03	Nil
3686	Z	4 28	0.74	0.60	Tr	0.02	Nil

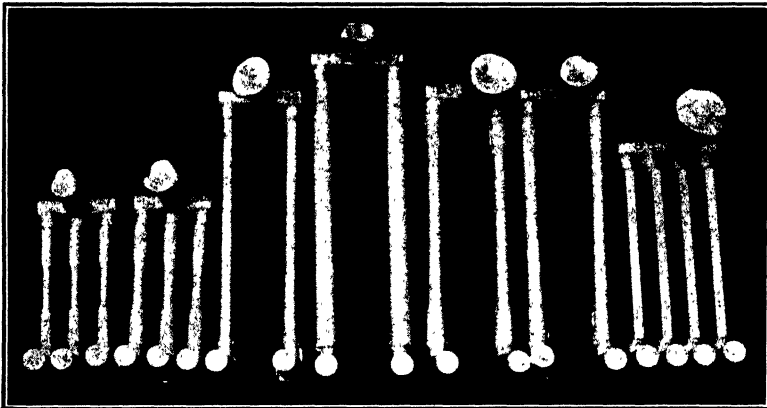


FIG. 2.—METHOD OF GATING USED BY ENGINEERING DIVISION (AIR SERVICE, U. S. A.).

The heat treatment given by the manufacturer is not known. Air Service Specification No. 11,300, to which this alloy as heat-treated was to conform, contains these requirements (paragraph 10):

(a) *Chemical Composition*.—Any composition containing not less than 90 per cent. aluminum will be acceptable provided the manufacturer shall state the composition he intends using and the chemical limits he can maintain

(b) *Physical Properties* (after heat treatment).—

Ultimate strength (minimum), pounds per square inch	29,000
Elongation in 2 in. (minimum), per cent.	4.5
Brinell hardness, about.	75-95

(c) *Specific Gravity*.—The specific gravity of this alloy shall not exceed 2.90.

PREPARATION AND MECHANICAL TESTING OF SPECIMENS

Tension

The TB1 tension test specimens, three to the mold, were cast to size (0.505 in. diameter and 2 in. gage length) and so tested; whereas the TB1A specimens were cast to $\frac{5}{8}$ in. diameter over the 2 in. gage length and then were machined to 0.505 in. diameter before testing, in order to give the properties of the material with the skin removed. The cross-sections were calculated on the least diameter normal to the parting line in the specimen. The test bars were held in V-wedge grips and were pulled in a 20,000-lb. Olsen machine. The percentage of elongation in 2 in. was measured with dividers to the nearest 0.01 in.

Shear

Four shear specimens $\frac{1}{2}$ in. in diameter by 2 in. long were machined from each mold of TB4 test specimens, two from the central portion of each bar. These shear specimens were inserted for test through $\frac{1}{2}$ -in. holes in three close-fitting shear die plates $\frac{3}{4}$ in. thick, and so assembled in a jig which secured the dies. The jig was then placed in a 50,000-lb. Olsen machine, where the load was applied to the middle shear plate, causing double shear at points $\frac{3}{4}$ in. apart. The ultimate strength in shear was determined by dividing the maximum load, in pounds, by twice the cross-sectional area of the specimen in square inches.

Compression

The compression specimens, which were $3\frac{5}{8}$ in. long with ends $\frac{3}{4}$ in. in diameter and center section reduced to $\frac{5}{8}$ in. diameter over a length of $2\frac{1}{2}$ in., were also machined from the central portion of TB14 bars $\frac{3}{4}$ in. round over the gage length and 13 in. long. To avoid lateral stresses, the compression specimens were tested in a rigid jig consisting of a heavy base and a strong post with a vertical guide-bearing 5 in. deep, which held the $1\frac{1}{2}$ -in. diameter plunger, which delivered the load vertically on top of the specimen. A 100,000-lb. Olsen machine was used in this test, the load being applied in 200-lb. increments. A Berry strain gage, reading to 0.0002 in. over a 2-in. gage length, was used to measure the deflection corresponding to each load. Although the stress-strain data thus derived served for the determination of the proportional limit, they were not dependable for the calculation of the compression modulus, because the specimens were too short.

Impact

The impact specimens were of the standard Charpy, round-notch type, machined to 0.394 in. square by 2.160 in. long, with a notch 0.197 in.

deep made by drilling to 0.078 in. diameter and milling out with a cutter of the same thickness. The net thickness of the specimen at the bottom of the groove was found by means of a special adapter measured together with the specimen in a micrometer caliper. This adapter is $\frac{1}{2}$ in. long and consists of a thin steel blade set in a base block perpendicularly to its back face and ground to an over-all thickness of 0.500 in. With the blade of the adapter in the groove of the specimen, the two are measured together. The net thickness of the specimen is this measurement less 0.500 in., the compensation for the adapter. Three specimens were machined from each of four bars in the standard TB6 (impact) mold. These bars were $\frac{9}{16}$ in. square by 9 in. long. The Charpy machine had anvils 1.575 in. apart and was equipped with a light steel hammer weighing 5.20 lb.; its radius to the center of gravity and the height of drop were, respectively, 26.0 and 50.3 in. The angular results were read to the nearest 0.5 degree and the energy absorbed was taken to the nearest 0.05 ft.-lb.

Torsion

The torsion specimens were cast two to the TB7 (torsion) mold, $1\frac{1}{4}$ in. in diameter by $15\frac{1}{2}$ in. long. These were machined down to 0.62 in. diameter over a length of $12\frac{1}{2}$ in., with $\frac{3}{4}$ in. diameter shoulders. The torsion tests were made in an Olsen machine of 3000 in.-lb. capacity, operated by hand. The specimens were held in toothed grips. The torsion-meter arms, each secured by two opposed points and a rest, were attached to the specimen at points spanning a 10-in. gage length. One of the arms bore an arc on a 12-in. radius, graduated in hundredths of an inch; and the other carried a pointer with a fine indicator point. The increments of torque, in inch-pounds, were recorded together with the corresponding angular increments of deflection in inches of arc. After the proportional limit had been amply exceeded, the instruments were removed and the specimens taken to failure. The modulus of rigidity and the proportional limit were calculated from the stress-strain curve. The ultimate strength in shear was found from the maximum torque moment,

in inch-pounds, $S_t = \frac{5.093T \text{ Max}}{\text{Diam.}^3}$ and the modulus of rigidity from the formula: $G = \frac{32 RLT}{\pi I^4 Z}$ where

- | | |
|----------------------------------|--|
| G = modulus of rigidity; | T = torque moment, in inch-pounds; |
| R = radius of torquemeter arc; | D = Diameter of specimen, in inches; |
| L = gage length on specimen; | Z = Angular deflection, in inches, on torquemeter arc. |

Tension Modulus

The tension-modulus specimens were cast two to the mold. The TB13 bars were cast to size, 0.75 in. in diameter over a 9-in. length, 13 in. long with S. A. E. threaded ends, 1 in. diameter. The TB14 modulus specimens were $\frac{7}{8}$ in. in diameter over a 9-in. length, 13 in. long, with $1\frac{1}{8}$ -in. shoulders. These bars, unlike the TB13 type, were tested as machined to 0.75 in. in diameter, with S. A. E. threaded ends. All tension-modulus specimens were held in a 20,000-lb. capacity Olsen machine by means of threaded adapters and self-aligning pulling bolts, 8 in. long. The loads were applied manually in increments of 200 lb. per sq. in., in accordance with loading tables previously calculated for the cross-section of each individual specimen. For each load the corresponding elongation was taken on a Ewing extensometer, which measured to 0.0002 in. over a gage length of 8 in. The proportional limit and modulus of elasticity in tension were taken from the stress-strain curve, the proportional limit as the point of tangency where the curve first changes slope. The percentage of elongation was found for 2, 4, and 8 in.

Hardness

Both Brinell and Rockwell hardness values were obtained on the tension, tension-modulus, and impact specimens. In the case of the first two types of specimen, the hardness tests were conducted on flats ($\frac{1}{4}$ in. wide or more) ground on the shoulders. A 10-mm. ball and a 500-kg. load applied for 30 sec. were used in the Brinell test, the impressions being read with a micrometer microscope having lateral travel. The Rockwell tests were made with a $\frac{1}{8}$ -in. diameter ball under a 100-kg. load applied for 10 sec.

Specific Gravity

One specific-gravity specimen (not machined) was taken to represent each of melts 3552, 3551, and 3686; the first melt as cast, the latter two as heat treated by the manufacturer. These specimens were cylinders $\frac{3}{4}$ in. in diameter by 2 in. long, weighing about 30 gm., and were cut from the end of TB1 tension specimens. They were sanded sufficiently to avoid air pockets during the standard test by the displacement method.

Metallography

From the grip end of one TB1 and one TB14 test specimen from each melt, a metallographic section was taken and polished. These were examined as unetched and as etched in the nitric acid quench for from 15

to 45 sec., in 2 per cent. aqueous hydrofluoric acid for 4 sec., and in acidified ferric chloride for from 10 to 15 sec. Special attention was paid to the effect of cross-section on grain size and on the quantity, size, and distribution of the hard compounds. The metallography at 1000 diameters was ascertained with a 2-mm. objective under oil immersion.

RESULTS

The data from the mechanical tests are embodied in Tables 1, 2, and 3. In these tables, the minimum and maximum values encountered

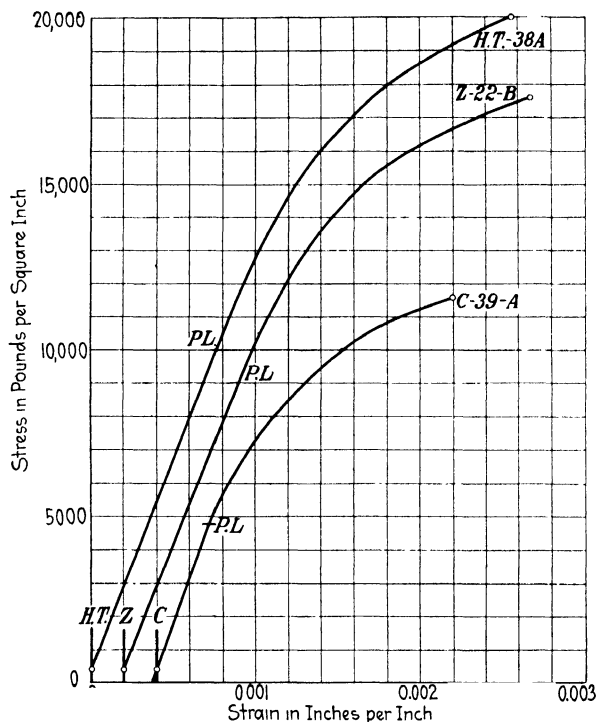


FIG. 3.—MODULUS OF ELASTICITY OF AL-CU-SI ALLOY AS CAST (TB13) TEST SPECIMENS: MELT 3551 (HT38A) HEAT TREATED, MELT 3686 (Z22B) HEAT TREATED, MELT 3532 (C39A) AS CAST. MODULUS OF ELASTICITY: HT38A, 10,000,000; Z22B, 9,800,000; C39A, 10,600,000. PROPORTIONAL LIMITS: HT38A, 10,000; Z22B, 9000; C39A, 4800. ULTIMATE STRENGTH, LB. PER SQ. IN.: HT38A, 31,600; Z22B, 24,500; C39A, 20,330.

are indicated together with the average of all specimens. Typical modulus curves, in tension, compression, and in torsion, for the material as cast and as heat treated are shown in Figs. 3 to 5, inclusive.

Metallographs, Figs. 6 to 9, inclusive, are unetched structures unless otherwise stated.

DISCUSSION OF RESULTS

Mechanical Testing

All the mechanical properties of the alloy as sand-cast were considerably improved by heat treatment, with the exception of the modulus values. On the whole, the range in properties for a given type and treatment of specimen was narrow. Comparison of the properties of machined and unmachined bars of the same diameter in the pure tension (TB1 and TB1A) specimens shows that the machined specimens were always inferior in strength, and generally in ductility, whether the speci-

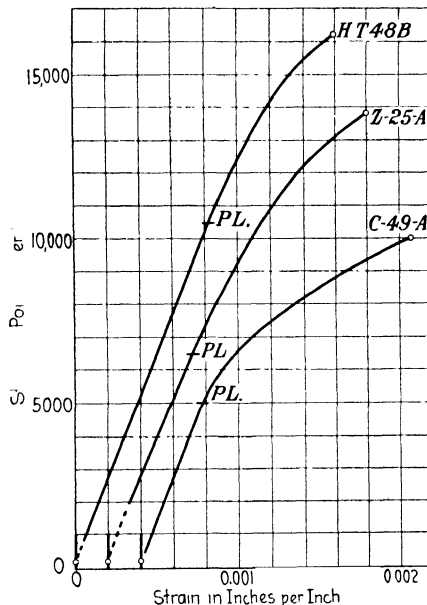


FIG. 4.—MODULUS OF ELASTICITY OF AL-CU-SI ALLOY, MACHINED (TB14) TEST SPECIMENS: MELT 3551 (HT48B) HEAT TREATED, MELT 3686 (Z25A) HEAT TREATED, MELT 3552 (C49A) AS CAST. MODULUS OF ELASTICITY: HT48B, 9,800,000; Z25A, 9,000,000; C49A, 10,000,000. PROPORTIONAL LIMITS, HT48B, 10,500; Z25A, 6500; C49A, 5000. ULTIMATE STRENGTH, LB. PER SQ. IN., HT48B, 26,900; Z25A, 20,960; C49A, 18,200.

mens were in the cast or in the heat-treated condition. In the tension-modulus (TB13) and (TB14) specimens, the machined were uniformly inferior in both strength and ductility, regardless of the condition of the alloy; but in the matter of proportional limit the superiority of the unmachined was not marked, except in one case (melt 3686). The tensile properties of the specimens of the smaller cross-sections were superior to those of bars of larger diameter. The ultimate strength in double shear was equivalent to that in tension, with machined

specimens the basis of comparison; and the strength and proportional limit in compression exceeded the corresponding properties in tension. The impact resistance of the alloy was at least doubled by heat treatment; and the impact value for the heat-treated alloy lower in copper content (melt 3686) was higher and appreciably different than when the percentage of copper was greater (melt 3551). The ultimate strength in torsion was practically the same as that (for similar bars) in tension when

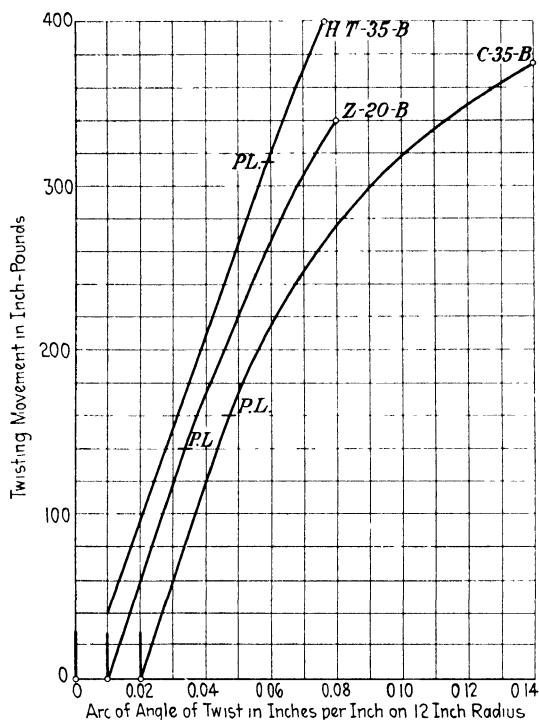


FIG. 5.—MODULUS OF RIGIDITY OF AL-CU-SI ALLOY, MACHINED (TB7) TEST SPECIMENS: MELT 3551 (HT35B) HEAT TREATED, MELT 3686 (Z20B) HEAT TREATED, MELT 3552 (C35B) AS CAST. MODULUS OF RIGIDITY: HT35B, 4,560,000; Z20B, 4,910,000; C35B, 4,840,000. PROPORTIONAL LIMITS: HT35B, 6570; Z20B, 2880; C35B, 3350. ULTIMATE STRENGTH, LB. PER SQ. IN. HT35B, 28,060; Z20B, 22,110; C35B, 19,390.

the specimens were in like condition. The proportional limits were, however, lower. The Brinell hardness of the cast alloy varied with the diameter of the specimen tested and ranged from 55 to 65; while that of the heat-treated alloy varied in the same fashion and from 68 to 84.

Unfortunately, no absolute valid comparison can be made concerning the effect of the method of gating on the mechanical properties resulting from this heat-treated material, because there is a variation between melts 3551 and 3686 of nearly 0.7 per cent. in copper content.

It would be predicted that for the same treatment and similar chemical composition otherwise, melt 3686, with 4.28 per cent. of copper, would attain lower strength and higher ductility than melt 3551, with 4.93 per cent. of copper. This is what actually obtained in the TB1 specimens.

It so happens, however, that the passable, but not high strength and ductility of the TB1 specimens from melt 3551, gated according to the method of the manufacturer, have been equalled or bettered by TB1 specimens cast as a remelt of bars from melt 3551, gated according to the Air Service method, and heat treated. The significance of this fact is that the two methods of gating and of heat treatment are in the main nearly equivalent. From this, it follows that the slightly inferior tensile

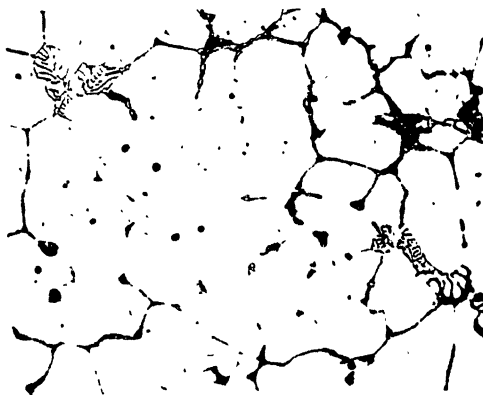


FIG. 6.—MELT 3552 AS SAND CAST; 21,450–2.2–63; CuAl_2 , Si, AND IRON-BEARING NEEDLES AND SKELETONS. $\times 100$.

properties of test specimens from melt 3686 (4.28 per cent. of copper), gated according to Air Service methods and treated by the manufacturer, may be taken to represent the low end of the range in properties that may be expected for the allowable commercial limits in chemical composition and from variations in heat treatment. The values from melt 3551 are not to be regarded as more than average; and for the high end of the range in commercially obtainable tensile properties, it may be assumed that 35,000 — 8.0 — 70 (ultimate strength — elongation — Brinell) is average for TB1 test specimens heat treated with castings.

Metallography

The structures of melts 3552, 3551, and 3686, shown in Figs. 6 to 9, inclusive, are illustrative of the effect of chemical composition and of heat treatment. Those of the TB14 test specimens, of large cross-sec-

tion, were the same as those of the TB1 bars. The rates of cooling were evidently equivalent.

As cast, melt 3552 contained CuAl_2 in triangular and, to less extent, in filigreed areas, often associated with iron-bearing needles and rounded



FIG. 7.—MELT 3551, AS HEAT TREATED; FeCl_3 REAGENT, 10 SEC.; 32,520-4.8-74; ROUNDED CuAl_2 , SOME Si, AND IRON-BEARING CONSTITUENTS. $\times 100$.

particles of silicon (Fig. 6). The iron-bearing needles were abundant, more so than the skeletons. Small elliptical groupings were also present (Fig. 6); these were composed of CuAl_3 , FeAl_3 , and X particles.



FIG. 8.—MELT 3686, AS HEAT TREATED; FeCl_3 REAGENT, 10 SEC.; 29,530-5.6-74; NOTE ABUNDANCE OF SKELETONS AND ABSENCE OF NEEDLES, AS COMPARED TO FIG. 8. $\times 100$.

Heat treatment caused the disappearance of CuAl_2 except in segregated areas, melt 3686, despite its lower copper content, containing considerably more of this compound undissolved than melt 3551. Both melts

had some undissolved silicon. Though the iron and silicon contents of the two were similar (0.8 and 0.6 per cent., respectively) iron-bearing skeletons and (well-defined) needles were found in melt 3551 (Fig. 7), but skeletons only (Fig. 8) in melt 3686. These skeletons were nearly all duplex, as shown in Fig. 9, consisting apparently of FeAl_3 (purple) and of X (watery blue gray). The former constituent, FeAl_3 , evidently was precipitated first. In many cases it looked doubtful whether X was a secondary product from the reaction of FeAl_3 with liquid, as is claimed by British investigators,² rather than a primary separation.



FIG. 9.—MELT 3686 (Z4B), AS HEAT TREATED; NITRIC-ACID QUENCH, 45 SEC.; SKELETON AT HIGH MAGNIFICATION SHOWING FeAl_3 DARK AND X LIGHT. $\times 100$.

In melt 3686, there was a considerably larger quantity of compounds than obtained in melt 3551. Inasmuch as by far the greater proportion of these hard constituents was of FeAl_3 and of X , which are ordinarily regarded as of minor solubility, their presence cannot be assigned to abnormalities in heat treatment and hardly to chemical composition, because melt 3686, with lower totality of copper, iron, and silicon, had a more abundant precipitate than melt 3551. The condition is more appropriately linked with alloying, melting practice, and rate of cooling. It seems likely, too, that this rather large residuum of compounds after heat treatment can have no beneficial effect on the mechanical properties of the material.

² Inst. Mechanical Engineers, Eleventh Report to the Alloys Research Committee (1921), 214.

TABLE 1.—Average Mechanical Properties of Aluminum-Copper-Silicon Alloy (Melt 3552) as Sand Cast

(Gated according to methods of manufacturer)

Type of Specimen	Mold Number	Number of Specimens	Ultimate Strength, Pounds per Square Inch	Proportional Limit, Pounds per Square Inch	Modulus, Pounds per Square Inch, $\times 10^3$	Elongation, Per Cent, in			Charpy Impact, Foot-pounds	Brinell Hardness, 500 Kg	Rockwell Hardness, $\frac{1}{8}$ -in Ball	Specific Gravity
						2 Inches	4 Inches	8 Inches				
TB1..... Tension, as cast	1-3	9	19,840 ^a 21,450 ^b 23,120 ^c			2 0 2 2 2 5				60 63 65	59 65 70	2.787
TB1A Tension, as machined	16-18	9	18,150 19,890 21,780			1 5 2 3 3 0				56 58 60	64 66 68	
TB4..... Double shear, as machined	27,28	8	18,400 19,220 19,780									
TB4..... Compression, as machined	29,30	6	34,290 35,060 35,320	5,220 6,780 7,820								
TB6..... Impact, as machined	32,33	24							1 10 1 40 1 70	55 58 60	66 71 83	
TB7..... Torsion, as machined	35,36	4	19,200 19,640 20,240	3,320 3,620 4,030	4,470 4,680 4,840							
TB13..... Tension, as cast	38-40	6	18,520 20,260 20,950	4,400 4,940 5,750	10,300 10,530 10,700	1 5 2 0 3 0	1 2 1 8 2 5	0 9 1 4 1 8		56 58 62	59 64 65	
TB14..... Tension modulus, as machined	49-51	6	17,800 18,370 19,150	4,250 4,750 5,000	9,800 9,980 10,300	1 0 1 8 2 5	0 8 1 6 2 0	0 6 1 3 1 8		55 60 63	58 59 62	

^a Minimum value encountered.^b Average value of all specimens^c Maximum value encountered

TABLE 2.—Average Mechanical Properties of Aluminum-Copper-Silicon Alloy (Melt 3551) as Heat Treated

(Gated according to methods of manufacturer)

Type of Specimen	Mold Number	Number of Specimens	Ultimate Strength, Pounds per Square Inch	Proportional Limit, Pounds per Square Inch	Modulus, Pounds per Square Inch, $\times 10^5$	Elongation, Per Cent., in			Charpy Impact, Foot-pounds	Brinell Hardness, 500 Kg	Rockwell Hardness, $\frac{1}{8}$ -in. Ball	Specific Gravity
						2 Inches	4 Inches	8 Inches				
TB1 Tension, as cast	1-6	18	29,800 ^a			3.5				69	71	2.794
			32,520 ^b			4.8				74	75	
			35,850 ^c			6.5				78	79	
TB1A Tension, as machined	15-18	12	29,220			4.5				73	76	
			31,280			5.5				75	81	
			33,380			6.5				78	85	
TB4 Double shear, as machined	26, 27	8	26,020									
			27,160									
			28,180									
TB4 Compression, as machined	28, 29	5	44,900	11,120								
			45,890	12,640								
			46,840	13,680								
TB6 Impact, as machined	32, 33	24							2.15	76	84	
									2.80	80	87	
									3.50	84	93	
TB7 Torsion, as machined	35, 36	4	28,060	6,570	4,430							
			29,640	6,920	4,530							
			31,760	7,090	4,590							
TB13 Tension as cast	38-40	6	25,300	9,500	10,000	2.5	3.2	3.4		68	78	
			29,420	9,920	10,440	3.9	3.9	3.9		73	80	
			35,050	10,000	10,900	4.5	4.2	4.4		78	83	
TB14 Modulus, as machined	48-50	6	26,070	8,800	9,500	2.0	1.8	1.9		66	71	
			26,980	9,920	9,710	3.3	2.9	2.6		70	76	
			28,900	11,000	9,900	4.0	4.0	3.5		73	81	

^a Minimum value encountered.^b Average value of all specimens.^c Maximum value encountered

TABLE 3.—Average Mechanical Properties of Aluminum-Copper-Silicon Alloy (Melt 3686) as Heat Treated

(Gated according to Air-Service methods)

Type of Specimen	Mold Number	Number of Specimens	Ultimate Strength, Pounds per Square Inch	Proportional Limit, Pounds per Square Inch	Modulus, Pounds per Square Inch, $\times 10^3$	Elongation, Per Cent., in			Charpy Impact, Foot-pounds	Brinell Hardness, 500 Kg.	Rockwell Hardness, $\frac{1}{8}$ -in. Ball	Specific Gravity
						2 Inches	4 Inches	8 Inches				
TB1. Tension, as cast	1-4	12	26,150 ^a 29,530 ^b 32,630 ^c			4.5 5.6 6.5				73 74 76	68 75 79	2.794
TB1A. Tension, as machined	10-11	6	21,300 23,970 25,530			2.0 3.3 5.0				69 72 75	75 79 81	
TB4. Double shear, as machined	15	4	24,470 25,430 26,310									
TB4. Compression, as machined	16	3	42,560 43,720 46,210	10,460 10,960 10,720								
TB6. Impact, as machined	17, 18	24							2.55 3.15 4.00	68 74 82	76 84 89	
TB7. Torsion, as machined	19, 20	4	22,100 22,750 23,560	2,880 3,120 3,500	4,650 4,820 5,040							
TB13. Tension modulus, as cast	22-24	6	20,860 24,330 25,760	7,750 8,570 9,200	9,700 9,820 9,900	3.5 4.0 4.5	2.0 3.1 3.8	1.2 2.1 2.8		72 78 82	69 76 74	
TB14. Tension modulus, as machined	25-27	6	20,960 21,190 22,420	5,750 6,100 6,500	9,000 9,120 9,450	2.5 2.9 3.5	2.2 2.2 2.2	1.6 1.7 2.2		64 69 74	65 71 76	

^a Minimum value encountered.
^b Average value of all specimens.
^c Maximum value encountered.

Effect of Reheating on the Al-Cu-Ni-Mg and the Al-Cu-Fe-Mg (Piston) Alloys

By SAMUEL DANIELS,* DAYTON, OHIO

(New York Meeting, February, 1926)

THE Al-Cu-Ni-Mg alloy is much benefited by heat treatment and, in such condition, is preferable to the Al-Cu-Fe-Mg alloy either as cast or as heat-treated, when both are reheated to temperatures of from 400° to 600° F. and compared, cold, with respect to strength and to hardness. The main differences between the alloys do not arise until the reheating temperature exceeds 400° F., above which they gradually soften. This softening is characterized metallographically by the appearance of intragranular precipitate. The Al-Cu-Ni-Mg alloy is weakest and least hard after being reheated at 600° F., the Al-Cu-Fe-Mg alloy at about 700° F. The former starts to reharden at 700° F., the latter at 800° F. There is a tendency for both alloys to lose strength and hardness with prolongation of time at the reheating temperatures of 500° and of 700° F. The Al-Cu-Ni-Mg alloy is considerably stronger and harder than the Al-Cu-Fe-Mg alloy when both are heat-treated and reheated for long periods of time at 500° and 700° F. Although the latter can be made harder initially than the Al-Cu-Ni-Mg alloy by suitable quenching and aging, heat treatment, in general, favors the retention of this initial (strength and) hardness after reheating to a much greater degree in the Al-Cu-Ni-Mg alloy. The percentage of elongation of the two materials in any condition is very small.

CERTAIN aluminum alloys have been used for pistons and other parts operating at temperatures up to 650° F. because of their lightness, high thermal conductivity and specific heat, fair strength and hardness at elevated temperatures, excellent machineability, and moderate resistance to corrosion. In the piston, the inertia forces and the bearing loading, and with this the vibration, are decreased. The piston head functions at a lower temperature (about 200° F. below one of cast iron), so that, because of the lessened tendency toward carbonization and detonation, higher compression ratios may be used. On the other hand, the aluminum alloys do not have the wearing and bearing qualities of cast iron; also they have a large coefficient of expansion, allowance for which must be made in the design.

The range in analyses of aluminum alloys, used for pistons in domestic and in foreign internal-combustion engines is shown in Table 1. There seem to be three general types of composition; one containing about 10

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per cent. of copper, from 0.5 to 1.4 per cent. of iron, from 0.2 to 0.6 per cent. of silicon, from nil to 0.35 per cent. of magnesium, and possibly with as much as 2.0 per cent. of zinc; one having from 7 to 8.5 per cent. of copper, with the ordinary impurities, and with or without a small quantity of tin and zinc; and one containing 4 per cent. copper, 2 per cent. nickel, 1.5 per cent. magnesium (Magnalite or "Y" alloy) type,¹ of which analysis there are several variations.

TABLE 1.—*Chemical Composition of Aluminum-Base Piston Alloys*

Engine or Source	Copper, Per Cent.	Iron, Per Cent.	Silicon, Per Cent.	Magnesium, Per Cent.	Manganese, Per Cent.	Zinc, Per Cent.	Tin, Per Cent.	Nickel, Per Cent.
Motor A (Am. auto.)	9 93	1 24	0.24	0 30				
Source A (Am. auto.)	10 0	1 25	0 3					
Motor B (Am. auto.)	10.0	0 5	0.3	0 25				
Source B (Am. auto and aero) . .	10 0	0.5	0 3					
Magnalite (Am. auto)	4 0	0 5	0 4	1 5				1 5
Liberty 12 (Am. aero)	10 0	1.25	0 4	0 25				2 25
Air-cooled Liberty 12 (Am. aero) .	4 0	0 5	0 3	1 5				2 0
Siddeley Puma (Br. aero)	11 60	0 76	0 26	Tr.	Nil	Nil	Nil	Nil
Rolls-Royce (Br. aero)	6 88	0.68	0 36	Tr.	Nil	Nil	Nil	Nil
Napier Lion (Br. aero)	6 90	0 38	0 21	Tr.	Nil	2 40	0 88	Nil
Hispano-Suiza (Fr. aero)	11 20	0 50	0 38	Tr.	Nil	0 67	Nil	Nil
B M W (Ger. aero)	10 42	1.22	0 59	0 11	Nil	2 00	Nil	Nil

These constituents have their peculiar effects on the alloy. Copper, which increases the strength and hardness at elevated temperature, is generally the predominating constituent alloyed with aluminum. Iron, nickel, manganese, and, in some cases, magnesium, intensify the effects conferred by the copper. In the 85 per cent. aluminum, 14 per cent. copper, 1 per cent. manganese piston alloy developed in England, the addition of the manganese causes a loss in thermal conductivity, which is restored by annealing. Zinc, however, decreases the hot strength and hardness substantially even at comparatively low temperature, and its presence therefore is not ordinarily desirable. This element often creeps in from the remelting of secondary material. Small amounts of tin are reported to improve both the soundness and the machineability. Foreign piston alloys during the war were far more variant in composition than those used in this country, a condition largely imposed by force of circumstance.

¹ Institute Mechanical Engineers, Eleventh Report to the Alloys Research Committee (1921). Rosenhain, Archbutt, and Wells: The Production and Heat-treatment of Chill Castings in an Aluminium Alloy ("Y"). *Jnl. Inst. Metal* (1923) **29**, 191.

Lyon and Daniels: Notes on a Sand-cast Aluminum-Copper-Nickel-Magnesium Alloy. *Jnl.*, S. A. E. (1924) **14**, 173.

PURPOSE OF INVESTIGATION

The present experimentation was conducted by the Material Section, Engineering Division, Air Service, U. S. Army, at McCook Field, Dayton, Ohio, and designed as preliminary research to compare the characteristics of the 92.5 per cent. aluminum, 4 per cent. copper, 2 per cent. nickel, 1.5 per cent. magnesium alloy with those of the 88.5 per cent. aluminum, 10 per cent. copper, 1.25 per cent. iron, 0.25 per cent. magnesium alloy. This paper deals with these piston materials when tested at room temperature after having been reheated both in the sand-cast and in the quenched and artificially aged condition to various temperatures and for different periods of time up to 50 hr. The following data do not include the mechanical properties of these alloys at elevated temperatures, which is the subject of a second investigation.

TABLE 2.—*Chemical Composition of Raw Materials and of Piston Alloys*

Metal	Melt	Where Used, Melt	Copper, Per Cent.	Nickel, Per Cent.	Iron, Per Cent.	Magnesium, Per Cent.	Silicon, Per Cent.	Aluminum, Per Cent.
Raw Materials								
Aluminum ingot.....	3240	3427	0.02		0.52		0.54	Balance
Aluminum ingot.....	3281	3639	0.24		0.40		0.37	Balance
Aluminum ingot.....	3769	3786	0.12		0.46		0.17	Balance
Al-Cu.....	3280	3427	49.78		0.38		0.24	Balance
Al-Cu-Ni.....	3345	3639	28.70	14.36	0.62		0.26	Balance
Al-Cu-Ni.....	3742	3786	28.98	14.40				Al-Fe-Si balance
Al-Cu-Fe.....	3095	3427	25.11		13.83			Al-Fe-Si balance
Mg Slab.....	2013	3427				95.5+		0.05
Mg Stick.....	3387	3639 & 3787			0.02	99.72	0.20	0.05
Piston Alloy Ingot								
Al-Cu-Ni-Mg.....	3639		4.48	2.10	0.72	1.47	0.30	Balance
Al-Cu-Ni-Mg.....	3786		4.13	1.79	0.58	1.38	0.24	Balance
Al-Cu-Fe-Mg.....	3427		9.66		1.38	0.28	0.40	Balance

MATERIAL

The two alloys, 92.5 per cent. Al, 4 per cent. Cu, 2 per cent. Ni, 1.5 per cent. Mg, and 88.5 per cent. Al, 10 per cent. Cu, 1.25 per cent. Fe, 0.25 per cent. Mg, were made from raw materials of high purity. The aluminum ingot conformed fairly closely to the requirements of Air Service Specification 11,010-B, Grade A (99.0 per cent. aluminum, minimum). The hardeners were made from commercial materials of highest purity and by approved methods. The Al-Cu-Ni hardener was so proportioned that the ratio of Cu to Ni was 2:1, as in the Al-Cu-Ni-Mg alloys itself, which assists in making up the charge. It would have been

possible to deal similarly with the Al-Cu-Fe hardener, but the ratio used enables another Air Service alloy to be made conveniently, so the one hardener serves a double purpose.

The alloys themselves were prepared in 300-lb. batches, the hardeners being melted down with the aluminum ingot. The metallic magnesium was added to the molten bath just before the pouring. The Al-Cu-Ni-Mg alloy was mixed in two lots, melts 3639 and 3786; while the Al-Cu-Fe-Mg alloy came in entirely from melt 3427. The analyses of the raw materials and the piston-alloy ingot are given in Table 2.

Air Service TBl tension specimens, cast to size (0.505 in. in diameter over a 2-in. gage length) and three to the mold (Fig. 1) were the standard



FIG. 1.—STANDARD AIR SERVICE TB-1 MOLD OF TENSION-TEST SPECIMENS.

for test. The properties of the alloys in such test bars, sand-cast from 1300° F., are as follows:

Alloy	Melt No.	Ultimate Strength, Lb per Sq In.	Elongation in 2 In., Per Cent.	Brinell 500 Kg.	Tested after Casting, Days
Al-Cu-Ni-Mg.....	3639	27,130	0.5	77	1
	3786	25,610	1.0	74	2
Al-Cu-Fe-Mg.....	3427	25,210	1.0	80	5
	3874	23,860	1.0	84	7

The fractures of the two alloys in any condition were distinguishable from one another. That of the Al-Cu-Ni-Mg alloy had a decidedly blue tinge and generally contained enough smooth crystal faces to give the surface a "snow-flaked" appearance. The fracture of the Al-Cu-Fe-Mg alloy was light gray, crystalline, and splintery.

PROCEDURE

Foundry

Fifty molds of TBI tension test specimens were sand-cast in the Al-Cu-Ni-Mg alloy in four lots: Molds 121 to 136, inclusive, as melt 3653; molds 137, 138, 139 and 40 as melt 3649—both melts being poured from melt 3639 ingot and gates from its remelting, in equal proportions; molds 1 to 15, inclusive, as melt 3866; and molds 16 to 30, inclusive, as melt 3867—both melts having a charge of equal parts of ingot from melt 3786 and of gates from its remelting.

Fifty molds were also sand-cast in the Al-Cu-Fe-Mg alloy, in five lots: molds 121 to 137, inclusive, as melt 3605; molds 138, 139 and 40, as melt 3606; and molds 1 to 12 inclusive, as melt 3873; molds 13 to 23, inclusive, as melt 3874; and molds 24 to 30, inclusive, as melt 3901. In charging these melts, equal parts of ingot from melt 3427 and of gates from its remelting were used.

The metal was melted in a plumbago crucible in an oil-fired furnace. From 30 to 45 min. were consumed in the melting operation, during which time the maximum furnace temperature was below 1350° F. in all cases except one (1400° F.). The pouring temperature was uniformly 1300° F. The molding sand was a coarse grade of Sandusky.

To facilitate the stamping of the test specimens, those in the Al-Cu-Ni-Mg alloy were stamped "N" and those in the Al-Cu-Fe-Mg alloy "F"; they were further identified by the proper mold and test specimen (A. B. C) number.

Chemical Analysis

The chemical composition was determined for the original ingot only.

Heat Treatment

The schedule of heat treatment is given as part of Tables 3 to 6 and was so planned that there would be ascertained for each alloy, both as sand-cast and as heat-treated, the effect of subsequent reheating at temperatures from 300° to 800° F. for 25 hr., and air-cooling (Table 3). A further purpose was to learn the effect of time at the reheating temperature of 500° and 700° F. when the alloys were initially in the sand-cast and in the heat-treated condition (Table 5). Long periods of soaking at elevated temperatures approximate conditions as they exist in the engine. Several other miscellaneous heat treatments were conducted in order to compare the equivalence of artificial aging processes (Table 6).

All tension specimens were placed on plates and were heated for quenching in an automatically controlled electric furnace, which could be held to within $\pm 10^\circ$ F. The Al-Cu-Ni-Mg alloy was soaked at 950° F.

for 5 hr., and the Al-Cu-Fe-Mg alloy at 925° F. for 5 hr., before being quenched into boiling water. They were both then aged at 212° F. in an automatically controlled electric oven. This procedure comprised the heat-treatment proper, which is denoted as "HT" in the various tables.

In this heat-treated (HT) and in the sand-cast (C) condition, the alloys were reheated, as outlined, in automatically controlled electric ovens and air-cooled after having been soaked at the required temperature for the desired length of time.

The specimens that were reheated in the sand-cast condition were not so reheated for from 2 to 7 months after having been cast, so this period of aging at room temperature elapsed before thermal treatment. The effect of this normal aging between the date of casting and that of reheating and between the date of casting and that of heat treatment (HT) proper will be considered later.

Mechanical Testing

After the completion of reheating and air-cooling, the specimens were allowed to rest at room temperature from 1 to 4 wk. before tensile and hardness testing. In the case of the results enumerated in Table 6, for instance, this period of normal aging before test (and after reheating) for molds 8, 9, 10, 11, 23, 24, 25, and 26 was 28 days; and for molds 12, 13, 14, 15, 28, 29, and 30 it was 15 days; molds 139 "N" and "F" were aged for 4 days before test.

A 20,000-lb. Olsen machine was used for the tension tests. The percentage of elongation was obtained by fitting the pieces of the ruptured test specimen closely together and by measuring with dividers to the nearest 0.01 in. the extension in 2 in. of gage length.

One Brinell hardness and two Rockwell hardness tests were made on the flattened smoothly ground surface of one-half of each broken test bar in each mold and on each of the individual hardness specimens. The Brinell test was made with a 10-mm. ball under a 500-kg. load, applied for 30 sec. and the Rockwell test with a 1/8-in. ball under a 100-kg. load and readings on the "B" scale. The hardness tests were made within 24 hr. after the tension tests.

All results recorded in Tables 3, 5, and 6 are the average of three or more specimens, as indicated, to the given condition. Where more than one mold (of three specimens) is shown for a particular treatment, it signifies that the additional molds were treated on separate occasions, but in like manner. When the fracture of broken specimens contained abnormal amounts of dross, the tensile properties were not included in the averages. The data in Table 4 concern only two Brinell tests made upon the same test bar at an interval of 5/8 in., the lapse of time between

tests being 9 months. Specific gravity tests were made by the displacement method on the belt-sanded grip ends of broken tension specimens.

Metallography

A $\frac{1}{2}$ -in. section was cut from the riser end of the middle B bar of such molds as seemed likely, judging from the tensile properties, to be of interest metallographically. Sections from 40N and F, 20N and F, 22N and F, 23N and F, 26N and F, 30N and F, 124N and F, 125N and F, 5N and F, 7N and F, 8N and F, and 11N and F were polished and examined both as unetched and as etched in the nitric acid quench for 4 and 30 sec.² and in 1 and 2 per cent. aqueous hydrofluoric acid solutions for 5 sec. The nitric acid reagent turns the CuAl_2 brown in 4 sec. and sometimes delineates the FeAl_3 and X (iron-bearing) constituents in 30 sec. It hardly affects the compound Mg_2Si . The hydrofluoric acid etchant reveals latent scratches, brings out the cored and grain structures, and tends to pit the matrix on long immersions. It stains NiAl_3 brown or black and restores, at least in part, the blue color of tarnished (black) Mg_2Si . Otherwise, the reagent has the effect of lessening the color contrast between CuAl_2 and T (the ternary compound of aluminum, copper, and nickel)³ and of heightening the purple color of the skeletons of FeAl_3 . It is not as desirable for photographic work as the nitric-acid quench. When a specimen, first etched in the hydrofluoric-acid solution, is subsequently etched in the nitric-acid quench, the dark stain is removed from NiAl_3 and the CuAl_2 is browned. The skeletons of the iron-bearing constituent are stained also. Neither of these reagents alone, with short immersions, affects the T constituent. The Al-Si eutectic was not found in any of the specimens.

The colors and characteristic forms of these constituents unetched and examined under tungsten daylo (blue) light are:

COMPOUND	COLOR	FORM
CuAl_2	Pinkish-white	Triangles or filigree
FeAl_3	Purple	Needles or skeletons
X	Watery-gray	Needles or skeletons
Mg_2Si	Blue	Needles, hexagons, or skeletons
NiAl_3	Smoky-gray	Needles or skeletons
$T(\text{Cu}_2\text{NiAl}_4)$	Blue-gray	Triangular areas or skeletons.

It is exceedingly difficult to distinguish between FeAl_3 and T and between X and NiAl_3 when unetched. The accompanying photomicrographs are of unetched structures unless otherwise stated.

² E. H. Dix, Jr.: Observations on the Occurrence of Iron and Silicon in Aluminum. *Trans.* (1923) **69**, 966.

³ Bingham and Houghton: The Constitution of Some Alloys of Aluminium with Copper and Nickel. *Jnl. Inst. Metals* (1923)**29**, 71.

TABLE 3.—*Effect of Reheating Temperatures on Both Cast and the Quenched and Aged* Piston Alloys*

Mold Number	Number of Specimens	Condition	Al-Cu-Ni-Mg Alloy				Al-Cu-Fe-Mg Alloy			
			Ultimate Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Brinell Hardness	Rockwell Hardness	Ultimate Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Brinell Hardness	Rockwell Hardness
40.....	3	As Cast (C)	28,410	0.5	96	84	27,330	0.5	98	84
17,136.....	6	C 300-25A†	28,260	0.5	94	92	25,880	0.6	100	92
18,135,137....	9	C 400-25A	28,090	0.6	89	90	26,170	0.5	96	92
19,132.....	6	C 500-25A	25,160	0.5	76	82	24,460	0.8	78	82
20,133.....	6	C 600-25A	21,180	1.4	58	64	22,720	1.2	66	69
21,134.....	6	C 700-25A	22,980	1.0	71	72	20,940	1.6	58	63
22.....	3	C 800-25A	26,860	1.0	82	82	25,980	1.2	71	77
124.....	3	As Heat Treated (HT)	35,460	1.0	101	95	36,120	0.7	99	94
2,126.....	6	HT 300-25A	38,910	0.6	102	94	36,770	0.6	114	98
3,130,138....	9	HT 400-25A	34,610	0.6	105	95	34,710	0.5	107	95
4,131.....	6	HT 500-25A	29,810	0.5	83	82	25,300	0.8	76	80
5,127.....	6	HT 600-25A	24,260	1.5	62	64	20,820	1.4	58	62
6,128.....	6	HT 700-25A	26,550	1.4	74	76	20,900	1.6	61	64
7.....	3	HT 800-25A	28,630	1.0	84	86	25,620	1.2	76	82

* Al-Cu-Ni-Mg alloy heat treatment (HT) = 950-5BW 16. Heated at 950° F. for 5 hr., quenched into boiling water, and aged at 212° F. for 16 hr. Al-Cu-Fe-Mg alloy heat treatment (HT) = 925-5BW 16.

† Cast, then reheated at 300° F. for 25 hr. and air cooled.

TABLE 4.—*Effect of Aging at Room Temperature on Stability of Brinell Hardness Impressed by Reheating at Various Temperatures for 25 Hr. and Air Cooling*

Condition of Specimen	Al-Cu-Ni-Mg Alloy			Al-Cu-Fe-Mg Alloy		
	Test Specimen Number	First Brinell Hardness	Brinell Hardness after 9 Mo	Test Specimen Number	First Brinell Hardness	Brinell Hardness after 9 Mo.
C 300-25A.....	136C	97	94	136B	100	101
C 400-25A.....	18A	85	87	18A	95	88
C 500-25A.....	19B	74	73	19B	79	79
C 600-25A.....	20A	58	58	20B	65	65
C 700-25A.....	21A	68	68	21A	57	59
C 800-25A.....	22C	80	77	Missing		
HT 300-25A.....	2A	101	97	2B	114	112
HT 400-25A.....	3A	104	101	3A	109	98
HT 500-25A.....	4A	84	80	4A	76	77
HT 600-25A.....	5A	61	59	5C	57	55
HT 700-25A.....	6A	74	71	128A	59	59
HT 800-25A.....	7B	85	84	7A	74	81

TABLE 5.—*Effect of Time at Reheating Temperature on Both Cast and Quenched and Aged Piston* Alloys*

Mold Number	Number of Specimens	Condition	Al-Cu-Ni-Mg Alloy				Al-Cu-Fe-Mg Alloy			
			Ultimate Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Brinell Hardness	Rockwell Hardness	Ultimate Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Brinell Hardness	Rockwell Hardness
23	3	C 500-1A	29,550	0.5	82	85	26,870	0.5	88	87
24	3	C 500-5A	26,240	0.5	78	74	26,940	0.5	85	82
25	3	C 500-15A	26,200	0.5	76	72	25,480	0.7	81	79
26	3	C 500-50A	25,270	0.5	70	74	25,130	0.7	77	79
27	3	C 700-1A	23,760	1.0	63	68	23,780	1.0	68	69
28	3	C 700-5A	22,220	1.1	62	61	22,520	1.2	60	57
29	3	C 700-15A	21,230	1.2	63	65	21,100	1.2	56	60
30	3	C 700-50A	21,850	1.8	60	61	19,700	1.0	55	57
8,139	6	HT 500-1A	33,210	0.5	100	92	34,800	0.5	99	93
9	3	HT 500-5A	35,920	0.5	92	90	28,690	0.5	89	94
10	3	HT 500-15A	31,590	0.5	88	84	25,430	0.5	77	77
11	3	HT 500-50A	28,770	0.5	79	80	23,350	0.5	71	73
12	3	HT 700-1A	27,720	1.0	66	65	22,100	0.9	61	65
13	3	HT 700-5A	27,520	1.5	70	69	20,730	1.2	56	57
14	3	HT 700-15A	26,450	1.3	69	73	19,070	1.2	55	58
15	3	HT 700-50A	25,410	1.7	70	69	20,460	1.6	54	56

* Al-Cu-Ni-Mg alloy heat treatment (HT) = 950 — 5BW 16. Al-Cu-Fe-Mg alloy heat treatment (HT) = 925-5BW 16.

TABLE 6.—*Effect of Miscellaneous Heat Treatments on Piston Alloys*

Mold Numbers*	Condition	Al-Cu-Ni-Mg Alloy				Al-Cu-Fe-Mg Alloy			
		Ultimate Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Brinell Hardness	Rockwell Hardness	Ultimate Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Brinell Hardness	Rockwell Hardness
121	HT† BW	33,660	1.0	98	92	34,280	1.0	94	90
122	HT-BW2	34,440	1.0	98	93	33,140	1.0	98	91
123	HT-BW 300-2	33,070	1.0	94	94	34,050	1.0	95	91
124	HT-BW 16	35,460	1.0	101	95	36,120	0.7	99	94
125	HT-BW 300-16	36,480	0.5	101	93	35,210	0.5	117	99
126	HT-BW16-300-25A	38,810	0.5	107	96	37,570	0.5	120	99
129	HT-BW300-16-300-25A	37,910	0.5	115	98	39,410	0.5	119	98

* Each mold contains three specimens.

† HT = Held at 950° F. for 5 hr. in the case of the Al-Cu-Ni-Mg alloy, and at 925° F. for 5 hr. in the case of the Al-Cu-Fe-Mg alloy.

RESULTS

The data in Tables 3 and 5 are plotted in Figs. 2 to 7; and the metallography of the two alloys is portrayed in Figs. 8 to 24.

Mechanical Properties of Alloys as Cast

The average properties of the two sand-cast-alloys as new melts and remelts tested as standard TBI tension bars within one week after casting are as follows:

Alloy	Number of Melts	Number of Specimens	Ultimate Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Brinell Hardness
Al-Cu-Ni-Mg.....	22	66	25,190	0.7	75
Al-Cu-Fe-Mg.....	10	45	25,430	1.0	80

The properties of the materials used for this investigation and tested under the same conditions correspond closely to these figures. The Al-Cu-Fe-Mg alloy is similar to the Al-Cu-Ni-Mg alloy in strength and in ductility but is somewhat harder; also the Al-Cu-Fe-Mg alloy, though having a range of about 2000 lb. per sq. in. in ultimate strength like the Al-Cu-Ni-Mg alloy, is considerably more erratic in hardness. The Al-Cu-Fe-Mg alloy, too, is about 3000 lb. per sq. in. stronger and about 20 Brinell numbers harder than the alloy supplied to Air Service Specification 11,024, which contains 10 per cent. of copper, less than 1 per cent. of iron, and no magnesium, while the two alloys have the same ductility.

Both the Al-Cu-Ni-Mg and the Al-Cu-Fe-Mg alloys are subject to change in properties with aging at atmospheric temperature after casting. For instance, these alloys (molds 40 N and 40 F) tested about 6 mo. after casting showed some increase in strength but appreciable enhancement of hardness; viz.,

Alloy	Number of Melt	Number of Specimens	Ultimate Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Brinell Hardness
Al-Cu-Ni-Mg.....	3653	3	28,410	0.5	96
Al-Cu-Fe-Mg.....	3605	3	27,330	0.5	98

This hardening is very likely a slow process, the accretion of hardness being gradual.

Mechanical Properties of Alloys as Quenched and Aged

The two alloys are much improved in strength and hardness by quenching and aging, but the ductility remains inappreciable:

Alloy	Heat Treatment	Number of Specimens	Ultimate Strength, Lb. per Sq. In.	Elongation, Per Cent. in 2 In.	Brinell Hardness	Specific Gravity
Al-Cu-Ni-Mg.....	950-5BW16*	3	35,460	1.0	101	2.73†
Al-Cu-Fe-Mg.....	925-5BW16	3	36,120	0.7	99	2.82†

* Heated at 950 for 5 hr. quenched into boiling water, and aged at 212° F. for 16 hr.

† Average of six melts.

In both alloys the accretion in strength is about 10,000 lb. per sq. in.; and in hardness, about 20 Brinell numbers.

With regard to the Al-Cu-Ni-Mg alloy, Air Service Specification 57-72-1 stipulates that TBI (unmachined) test specimens heat-treated with castings shall have a minimum ultimate strength of 32,000 lb. per sq. in. and a minimum Brinell hardness of 90. Through the heat treatment indicated above, the alloy readily meets these requirements; but as the operation consumes 21 hr. exclusive of the time necessary to attain temperature and of that devoted to manipulation, it was deemed advisable to curtail the process in some way. Recent work has proved that a 950-4BW 400-1 treatment, easily effected in a working day, may be substituted for the 950-5BW 16 rationale, with equivalent results in strength and in elongation and with some advance in hardness.

The Al-Cu-Fe-Mg alloy may be quenched and aged to develop greater hardness than the Al-Cu-Ni-Mg alloy for about the same strength and percentage of elongation. A treatment such as 925-5BW 300-16 will result in a hardness of 115 or more (See Table 6).⁴ A shorter, equivalent heat treatment, similar to that described for Al-Cu-Ni-Mg alloy, has been made available. On the whole, the high-copper alloy does not respond to heat treatment so reliably as the nickel-bearing material, which is also somewhat lower in specific gravity.

Effect of Reheating Temperature upon Mechanical Properties

In Figs. 2, 3, and 4 are plotted the data relative to the effect of reheating, after casting and after quenching and aging, at the temperatures of 300°, 400°, 500°, 600°, 700°, and 800° F. for 25 hr. followed by air cooling.

Sand-Cast Alloys.—Fig. 2 illustrates the effect of reheating on the alloys as sand-cast (Table 3). It will be observed that both materials have been ascribed an ultimate strength of about 28,000 lb. per sq. in., an elongation of 0.5 per cent., and Brinell and Rockwell values of about 95 and 85, respectively. These values were inserted, rather than the figures given for the alloys shortly after casting, because they represent the alloys as aged at room temperature for about 6 mo. Such values serve as a better base, for the other molds listed in Tables 3, 5, and 6 were aged in the cast condition for from 2 to 6 mo. before being reheated or before being quenched and artificially aged and then reheated.

Neither the Al-Cu-Ni-Mg nor the Al-Cu-Fe-Mg alloy, on reheating, lost much of its initial strength as sand-cast until heated at 500° F. The Al-Cu-Ni-Mg alloy was weakest after cooling from 600° F., when its strength was about 21,000 lb. per sq. in.; whereas the Al-Cu-Fe-Mg

⁴ Samuel Daniels: The Heat Treatment of the Al-Cu-Fe-Mg (Piston) Alloy: *Forging—Stamping—Heat Treating* (1925) 2, 346.

attained a similar minimum strength after treatment at 700° F. Reheating to temperatures beyond which these minima were obtained caused a rather sharp upturn in strength. The curves of hardness were parallel in trend to those of ultimate strength. In both alloys, the hardness values declined from maxima of about 97 Brinell and 85 Rockwell, as sand-cast, to corresponding minima of about 58 and 64, which the Al-Cu-Ni-Mg alloy reached with the draw at 600° F. and the Al-Cu-

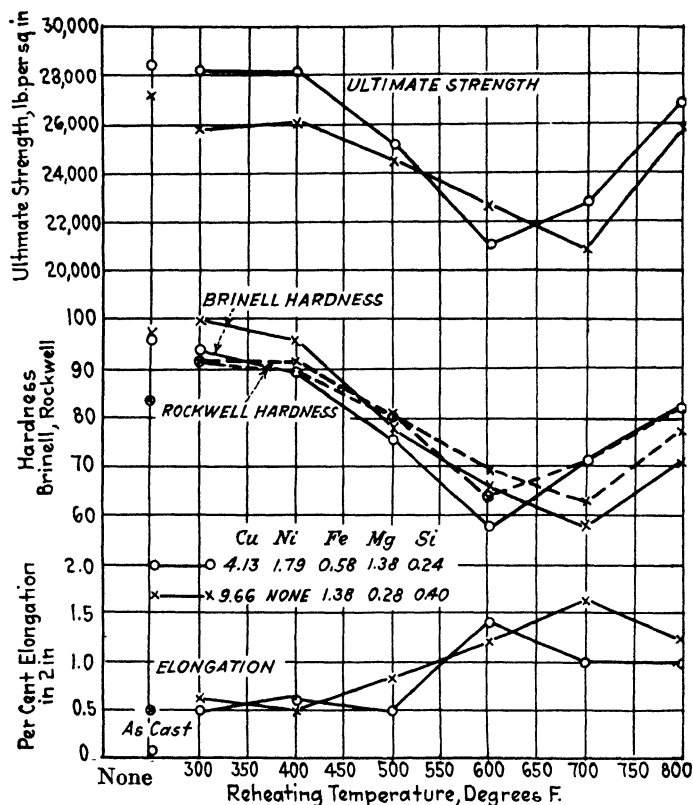


FIG. 2.—EFFECT ON SAND-CAST PISTON ALLOYS OF REHEATING AT INDICATED TEMPERATURES FOR 25 HR. AND THEN AIR COOLING.

Fe-Mg alloy with that at 700° F. Once having attained their minima, both alloys made a sharp upturn in hardness, but the Al-Cu-Ni-Mg alloy hardened more intensely, with the result that after the draw at 800° F. it had Brinell and Rockwell hardness of 82; while the Al-Cu-Fe-Mg alloy recuperated to like properties of 71 and 77, respectively. As to elongation that of the nickel-bearing alloy remained unchanged at 0.5 per cent. until the material was reheated to 600° F. when it made a maximum of 1.4 per cent. The alloy high in iron content acted similarly and acquired its maximum elongation, 1.6 per cent., when drawn at 700° F.

With reheating temperatures beyond those at which the maximum of elongation was obtained, both alloys lost in ductility; but when cooled from within the reheating range of from 400° to 600° F. the two materials were not appreciably different in ductility or hardness for a given drawing temperature. After reheating at 500° F., they had identical properties—an ultimate strength of about 25,000 lb. per sq. in., an elongation of about 0.6 per cent. a Brinell hardness of approximately 77, and a Rockwell hardness of 82. Drawn at 400° F., the Al-Cu-Ni-Mg alloy was the stronger by about 2000 lb. per sq. in.; and drawn at 600° F., the Al-Cu-Fe-Mg alloy was superior by a similar amount. The properties of the alloys after having been drawn at 800° F., when compared with those of the material as sand-cast, showed that neither alloy suffered much loss in strength but both were improved in ductility. At the same time the Al-Cu-Ni-Mg alloy lost about 15 per cent. and the Al-Cu-Fe-Mg alloy about 30 per cent. of its original Brinell hardness.

Quenched and Aged Alloys.—The effect of reheating on the sand-cast alloys in the heat-treated condition is shown in Table 3 and Fig. 3. As quenched and artificially aged both alloys possessed an ultimate strength of about 36,000 lb. per sq. in., an elongation of about 1 per cent., a Brinell hardness of 100, and a Rockwell hardness of 95. With increase in temperature of reheating above about 400° F., both alloys rapidly lost strength and hardness (original or acquired) down to a minimum with the draw at 600° F., after which the Al-Cu-Ni-Mg alloy had an ultimate strength of 24,250 lb. per sq. in., a Brinell hardness of 62, and a Rockwell hardness of 64; and the Al-Cu-Fe-Mg alloy attained an ultimate strength of 20,820 lb. per sq. in., a Brinell hardness of 58, and a Rockwell hardness of 62. The Al-Cu-Ni-Mg alloy attained a maximum hardness with the reheat at 400° F., and the Al-Cu-Fe-Mg alloy reached its peak at 300° F. With reheating at 700° F., the former alloy regained some strength and proportionately more hardness; whereas the latter alloy made negligible recovery from its minima. As in the case of the sand-cast alloys, reheating quenched and aged specimens to temperatures of 700° and 800° F. caused the Al-Cu-Ni-Mg alloy to harden more intensely than the Al-Cu-Fe-Mg alloy; the former hardened above 600° and the latter above 700° F.

A comparison shows that, with the exception of the draw at 400° F., after which the strength of both alloys was approximately 35,000 lb. per sq. in. and the Brinell hardness about 106, the Al-Cu-Ni-Mg alloy for the entire range of reheating temperatures was superior in strength to the Al-Cu-Fe-Mg alloy by from 2000 to 4000 lb. per sq. in. The difference in hardness was not great until, for reheating temperatures above 600° F., it was in favor of the nickel-bearing alloy. As air-cooled from the drawing temperature of 800° F., the Al-Cu-Ni-Mg alloy had 80 per cent. and the Al-Cu-Fe-Mg alloy about 70 per cent. of the strength and Brinell hardness they possessed as quenched and aged only.

The heat-treated Al-Cu-Ni-Mg and Al-Cu-Fe-Mg alloys did not gain in ductility until drawn at temperatures in excess of about 500° F., as in the case of the sand-cast materials. When both alloys had the minimum strength and hardness, their elongations were maximum at about 1.5 per cent. When the alloys began to harden, at 700° and at 800° F.

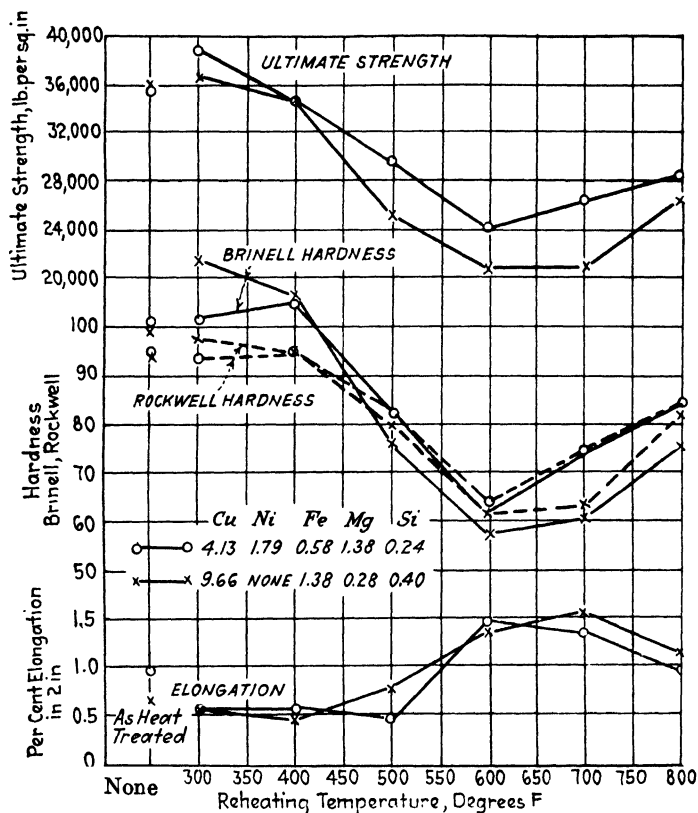


FIG. 3.—EFFECT ON SAND-CAST AND HEAT-TREATED PISTON ALLOYS OF REHEATING AT INDICATED TEMPERATURES FOR 25 HR. AND THEN AIR COOLING.

respectively, the percentage of elongation tended to decline somewhat from the maximum.

Fig. 4 shows more clearly the effect reheating exerted on both the sand-cast and the cast and heat-treated alloys. The Al-Cu-Ni-Mg alloy was appreciably stronger and slightly harder in the heat-treated than in the sand-cast condition whatever the drawing temperature. For the Al-Cu-Fe-Mg alloy, there appeared, from the standpoints of strength and hardness, to be no valid reason for heat-treating when the material is to be subjected to reheating temperatures in excess of 400° F.

Of course, heat treatment might be desirable with a view toward removing growth and improving the machineability. Inasmuch as the operating temperature of aeromotive piston heads may be taken to range between 400° and 600° F., the Al-Cu-Ni-Mg alloy in the heat-treated (quenched and aged) condition would be preferable to the Al-Cu-Fe-Mg alloy in similar condition, and with reference to strength at normal (room) temperature after cooling. The difference in hardness in favor of the former alloy was not pronounced except when the reheating temperature was 700° or 800° F.

With reference to what uniformity in strength resulted from the duplicate heat treatments, enumerated in Table 3 and discussed as averages in the preceding paragraphs, it should be said that in all cases except

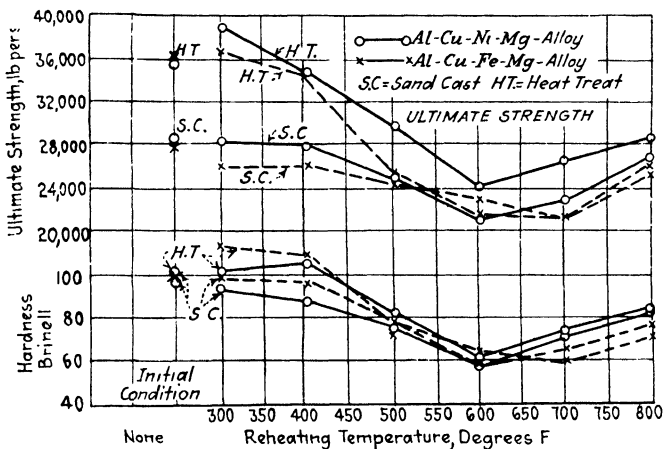


FIG. 4.—EFFECT ON THE ULTIMATE STRENGTH AND BRINELL HARDNESS OF PISTON ALLOYS AS SAND-CAST AND AS HEAT-TREATED OF REHEATING AT INDICATED TEMPERATURES FOR 25 HR. AND THEN AIR COOLING.

two molds the numerical differences were generally less than 10 per cent., which is within the allowable experimental error. Moreover, it was not important whether the alloys were tested one week or one month after reheating and air-cooling. The effect of longer periods of aging at atmospheric temperature (following reheating) on the stability of the tensile properties was not ascertained, but Brinell hardness tests made on individual test bars 9 months after the first test indicated a pronounced degree of permanence, whatever the reheating temperature (Table 4).

Effect of Time at Reheating Temperature upon Mechanical Properties

Figs. 5, 6, and 7 show the mechanical properties of the alloys in both the cast and the quenched and aged conditions and subsequently reheated for various periods up to 50 hr. at temperatures of 500° and of 700° F., followed by air-cooling.

The heat-treated Al-Cu-Ni-Mg and Al-Cu-Fe-Mg alloys did not gain in ductility until drawn at temperatures in excess of about 500° F., as in the case of the sand-cast materials. When both alloys had the minimum strength and hardness, their elongations were maximum at about 1.5 per cent. When the alloys began to harden, at 700° and at 800° F.

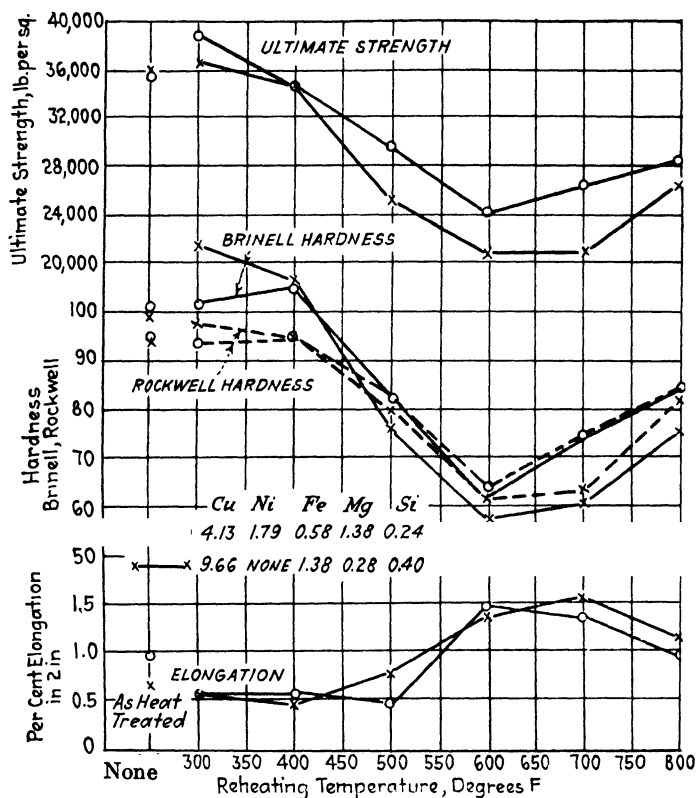


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Of course, heat treatment might be desirable with a view toward removing growth and improving the machineability. Inasmuch as the operating temperature of aeromotive piston heads may be taken to range between 400° and 600° F., the Al-Cu-Ni-Mg alloy in the heat-treated (quenched and aged) condition would be preferable to the Al-Cu-Fe-Mg alloy in similar condition, and with reference to strength at normal (room) temperature after cooling. The difference in hardness in favor of the former alloy was not pronounced except when the reheating temperature was 700° or 800° F.

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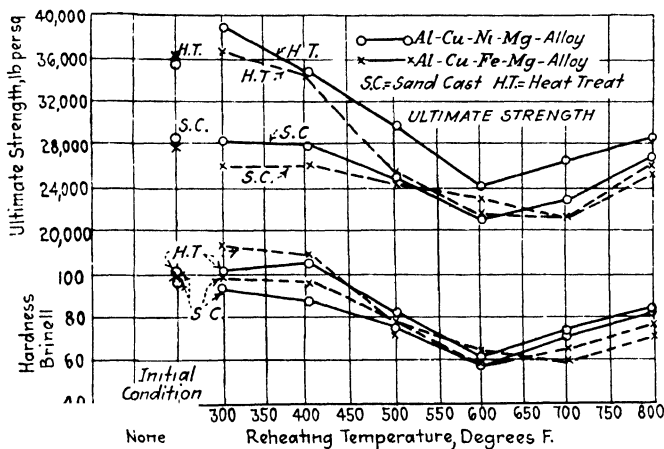


FIG. 4.—EFFECT ON THE ULTIMATE STRENGTH AND BRINELL HARDNESS OF PISTON ALLOYS AS SAND-CAST AND AS HEAT-TREATED OF REHEATING AT INDICATED TEMPERATURES FOR 25 HR. AND THEN AIR COOLING.

two molds the numerical differences were generally less than 10 per cent., which is within the allowable experimental error. Moreover, it was not important whether the alloys were tested one week or one month after reheating and air-cooling. The effect of longer periods of aging at atmospheric temperature (following reheating) on the stability of the tensile properties was not ascertained, but Brinell hardness tests made on individual test bars 9 months after the first test indicated a pronounced degree of permanence, whatever the reheating temperature (Table 4).

Effect of Time at Reheating Temperature upon Mechanical Properties

Figs. 5, 6, and 7 show the mechanical properties of the alloys in both the cast and the quenched and aged conditions and subsequently reheated for various periods up to 50 hr. at temperatures of 500° and of 700° F., followed by air-cooling.

Sand-cast Alloys.—Fig. 5 represents graphically the data, from Table 5, on the effect on the sand-cast alloys of time at reheating temperatures of 500° and 700° F., the points being derived from the averages of three test specimens. For the draw at 500° F., the strength of both alloys after the 1-hr. treatment was about the same as that of both as cast, though the hardness was lower. After having been drawn at 500° F. for 5 hr., the two materials had an ultimate strength of about 26,000

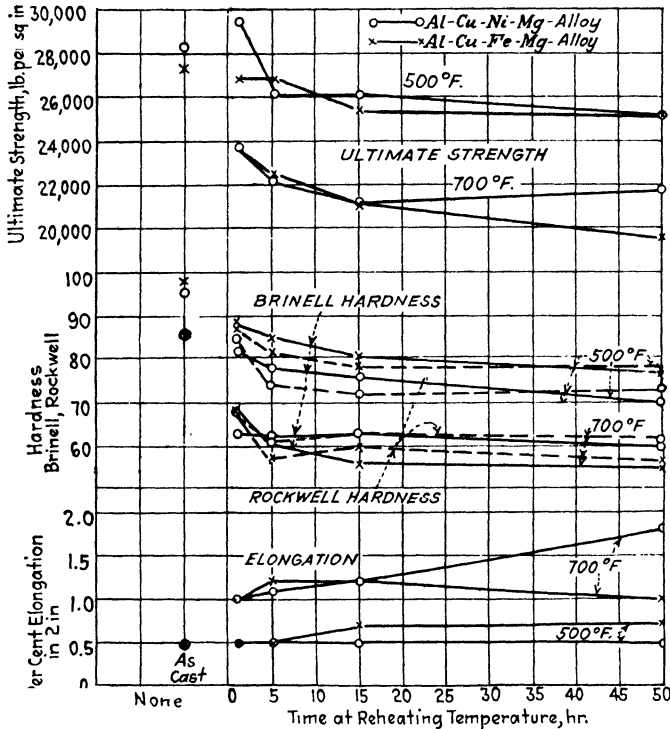


FIG. 5.—EFFECT ON SAND-CAST PISTON ALLOYS OF HEATING, AFTER CASTING, AT 500° AND 700° F. FOR INDICATED PERIODS OF TIME AND THEN AIR COOLING.

lb. per sq. in., which persisted practically intact for drawing periods up to 50 hr. The Al-Cu-Fe-Mg alloy had somewhat greater hardness than the Al-Cu-Ni-Mg alloy for all drawing periods. The treatment at 700° F. in one hour caused the strength of the alloys to decline to 24,000 lb. per sq. in., the hardness to about 65 Brinell and 69 Rockwell, and the elongation to increase to 1.0 per cent. With increase in time up to 50 hr. at this drawing temperature, the Al-Cu-Fe-Mg alloy continued to lose strength and hardness, though its ductility did not change perceptibly; the Al-Cu-Ni-Mg alloy roughly paralleled this performance except for the 50-hr. draw, which left it stronger, harder, and more ductile than

the Al-Cu-Fe-Mg alloy. The Al-Cu-Ni-Mg alloy, after the 50-hr. draw, was as strong as after the 15-hr. draw. Taken as a whole, the two alloys in the sand-cast condition on being reheated at 500° and at 700° F. for periods up to 50 hr., and then air-cooled, reacted in much the same manner.

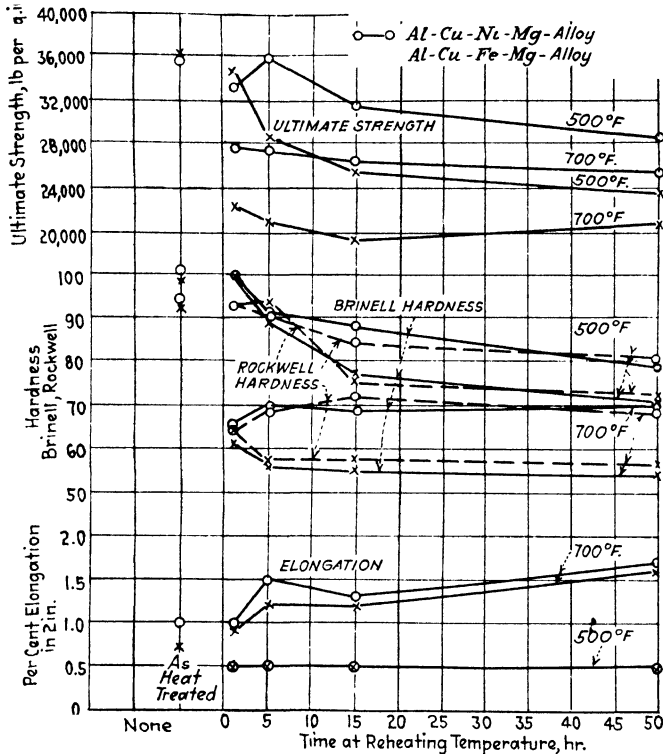


FIG. 6.—EFFECT ON SAND-CAST AND HEAT-TREATED PISTON ALLOYS OF HEATING, AFTER HEAT TREATMENT, AT 500° AND 700° F. FOR INDICATED PERIODS OF TIME AND THEN AIR COOLING.

Quenched and Aged Alloys.—When in the heat-treated condition, however, reheating at 500° and at 700° F. for various soaking periods and air-cooling brought out distinct differences in the behavior of the alloys. The averages for three test bars indicated (Fig. 6) that whereas heating at 500° F. for 1 hr. did not appreciably alter the properties of the alloys as heat-treated, further soaking was accompanied by a drop from about 34,000 lb. per sq. in., 0.5 per cent. elongation, and 100 Brinell hardness in both alloys gradually to an ultimate strength of 29,000 lb. per sq. in., an elongation of 0.5 per cent. and a Brinell hardness of 80 in the Al-Cu-Ni-Mg alloy and precipitately (and then gradually) to an

ultimate strength of 23,000 lb. per sq. in., an elongation of 0.5 per cent. and a Brinell hardness of 70 in the Al-Cu-Fe-Mg alloy, with increase in time at reheating temperature up to 50 hr. The hardness curves in the main followed the trend of the curves of ultimate strength; and the percentage of elongation remained unchanged whatever the soaking period. As in the case of the drawing experiments at 500° F., the Al-Cu-Ni-Mg alloy was stronger by 5000 lb. per sq. in. or more and considerably harder than the Al-Cu-Fe-Mg alloy when drawn at 700° F. for any length of time at the reheating temperature up to 50 hr. When drawn for 1 hr. at 700° F., the former alloy had an ultimate strength of about 28,000 lb. per sq. in. and a Brinell hardness of 66; and the latter, a strength of 22,100 lb. per sq. in. and a Brinell hardness of 61. Longer drawing periods caused the Al-Cu-Ni-Mg alloy to forfeit slight additional strength but not its hardness (of about 70 in both Brinell and Rockwell) and the Al-Cu-Fe-Mg alloy to act similarly with regard to strength but to relinquish still more of its hardness (down to about 55 in both Brinell and Rockwell). Both alloys concomitantly gained in ductility.

Fig. 6 also shows that, disregarding the concordant percentages of elongation, the Al-Cu-Ni-Mg alloy was quite superior in strength and in hardness to the Al-Cu-Fe-Mg alloy when heat-treated and then reheated at 500° or at 700° F. for periods up to 50 hr. and then air-cooled. Furthermore, the Al-Cu-Ni-Mg alloy drawn at 700° F. for 15 hr. up to 50 hr. was practically equivalent in strength and in hardness to the Al-Cu-Fe-Mg alloy treated for the same range of time at 500° F. This condition is probably induced by two factors: The inherently greater strength of the Al-Cu-Ni-Mg alloy when heat-treated and drawn at temperatures in excess of 400° F.; and the ability of the Al-Cu-Ni-Mg alloy to air-harden from 700° F., which potentiality does not reside in the Al-Cu-Fe-Mg alloy, whether in the cast or in the heat-treated form, until a temperature of 800° F. is reached (Figs. 2 and 3, and Table 3). The hardening of the Al-Cu-Ni-Mg alloy from 700° F. might be of importance should the pistons be subjected to excessive head temperatures. (In the case of heat-treated Al-Cu-Ni-Mg alloy cylinder heads shrunk on steel liners, it would be advisable to use a shrinking temperature of 700° F. and thus take advantage of the gain in strength caused by air-hardening.)

Fig. 7 illustrates comparatively the effect of time at reheating temperatures of 500° and of 700° F. on the ultimate strength of the piston alloys as sand-cast and as heat-treated. Both alloys were stronger in either condition when drawn at 500° than when drawn at 700° F. regardless of period. The Al-Cu-Ni-Mg alloy, heat-treated and drawn at 700° F. was not better, however, than when as sand-cast and drawn at 500° F. As sand-cast and drawn at 700° F., the alloy was at its worst. The Al-Cu-Fe-Mg acted still differently. Given reheating temperatures

of 500° or 700° F. and the more pertinent reheating periods of 5 hr. or over, whether the alloy was initially as sand-cast or as heat-treated before reheating was of minor importance (from the standpoint of strength). For extended periods of reheating at 500° F., the material as sand-cast tended to be somewhat better than as heat-treated; and for nearly all periods at 700° F., the same direction of superiority was evident.

Interpretation of the foregoing data in the light of the utility of these two alloys as piston materials demands, first, the recognition of the fact that they do not consider mechanical properties at the operating temperatures themselves, which point is being made the subject of another investigation. If, then, the characteristics of the alloys are compared

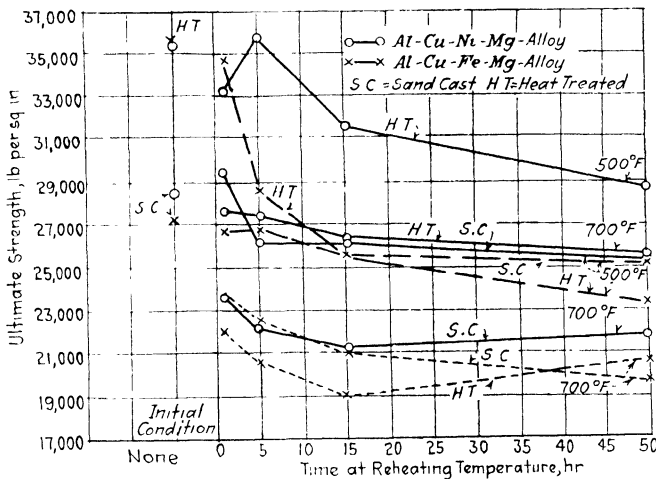


FIG. 7.—EFFECT ON ULTIMATE STRENGTH OF SAND-CAST AND HEAT-TREATED PISTON ALLOYS OF REHEATING AT 500° AND 700° F. FOR INDICATED PERIODS OF TIME AND THEN AIR-COOLING.

only after they have been cooled to room temperature following reheating in either the sand-cast or in the quenched and aged condition, certain generalizations may be made.

Assuming that the operating temperature of aeromotive piston heads ranges between 400° and 600° F., and that the skirt (from the piston-ring lands down) functions at temperatures below 300° F., the Al-Cu-Ni-Mg alloy in the heat-treated condition is preferable, from the standpoint of the strength and hardness of the head, to the Al-Cu-Fe-Mg alloy, either as cast or as heat-treated. Hardness of the skirt is, of course, essential to proper bearing qualities. This would be conferred on either alloy by heat treatment, which seems, mechanically, to be more advisable in the case of the Al-Cu-Ni-Mg alloy than in that of the Al-Cu-Fe-Mg

alloy. The machining properties and bearing qualities of both alloys are also improved by quenching and aging, and the resulting smoother surfaces may hinder carbon deposition and burning of the piston.

From another angle, some insight may be gained as to engine performance through examination of the pistons after they have been in service. Inasmuch as their hardness on cooling has been shown, within certain limits, to be a function of the temperature to which they have been heated, and of the time thereat, it is possible to gage approximately their operating temperature. Then, too, some indication is given as to the nature of the heat transfer and concerning the preservation of the hardness of the skirt, which is an essential to effective functioning of the piston.

METALLOGRAPHY

The metallography of the alloys at low magnification is illustrated in Figs. 8 to 11. Figs. 12 to 24 inclusive, are at either 500 or 1000 diameters, the latter having been photographed under oil immersion.

Sand-cast Alloys

As sand-cast, the Al-Cu-Ni-Mg alloy (Figs. 8 and 12) had a rather open network, a small amount of CuAl_2 either as filigree or in triangular areas, a rather more conspicuous amount of Mg_2Si in skeletons or in filigree, a large amount of NiAl_3 (often segregated) in stringers, needles, or rippled skeletons, slightly less of T , the ternary compound of aluminum, copper, and nickel, and still less of FeAl_3 in the form of skeletons, hardly to be distinguished from T . A few needles of X (iron-silicon-aluminum?) compound were also observed. The matrix contained no intragranular precipitate.

The structure of the Al-Cu-Fe-Mg alloy as sand-cast was not so complex (Figs. 9 and 13). It had a larger amount of intergranular compounds than the Al-Cu-Ni-Mg alloy and a more complete network. The principal constituent was CuAl_2 , generally in triangular patches, but occasionally filigreed. The high iron (1.25 per cent.) content was revealed in the form of two constituents: FeAl_3 skeletons, in moderate amount, and needles of X in comparative abundance. Often these two compounds were closely associated as duplex particles. Both the copper and the iron-bearing compounds tended to segregate. The compound Mg_2Si was present in small film-like areas and sometimes intimately associated with CuAl_2 . No intragranular precipitate was observed.

As cast and reheated at 600° F. for 25 hr. and air-cooled, the Al-Cu-Fe-Mg alloy was unchanged in structure except for the appearance of a

finely divided intragranular precipitate (Fig. 15) and the Al-Cu-Ni-Mg alloy was traversed by fine markings (Fig. 14), which could not be posi-

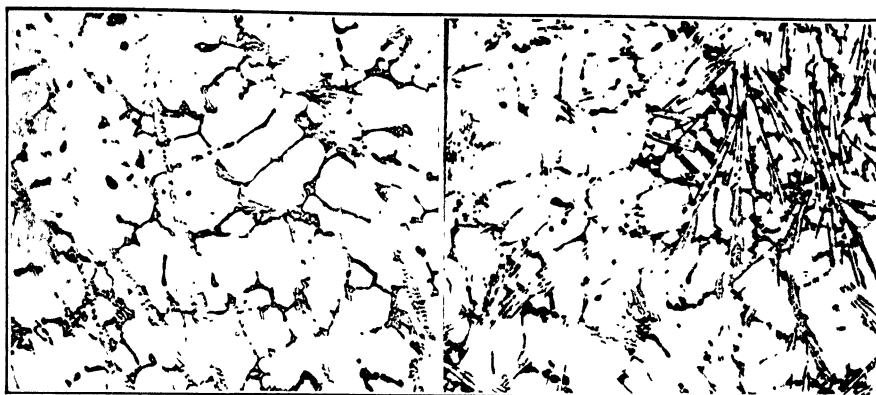


FIG. 8.

FIG. 9.

FIG. 8.—AL-CU-NI-MG ALLOY AS SAND-CAST; 2 PER CENT. AQ H_2F_2 , 5 SEC. $\times 100$. Ultimate strength 28,410 lb. per sq. in., Brinell hardness 96; elongation 0.5 per cent. Stringers of $NiAl_3$, skeletons of $FeAl_3$ (?) and of T , and some $CuAl_2$ and Mg_2Si form incomplete network.

FIG. 9.—AL-CU-Fe-MG ALLOY, AS SAND-CAST; NITRIC-ACID QUENCH, 8 SEC. $\times 100$. Ultimate strength 27,330 lb. per sq. in.; Brinell hardness 98; elongation 0.5 per cent. $CuAl_2$ (black) and skeletons and needles of Fe-bearing compounds.

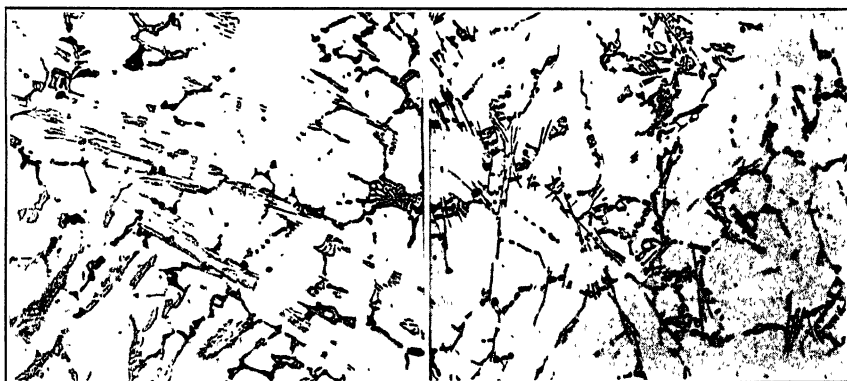


FIG. 10.

FIG. 11.

FIG. 10.—AL-CU-NI-MG ALLOY; 950-5BW 16; 1 PER CENT. AQ H_2F_2 , 5 SEC. $\times 100$. Ultimate strength 35,460 lb. per sq. in.; Brinell hardness 101, elongation 0.5 per cent. Some $NiAl_3$ rounded, T rounded and in clumps, $CuAl_2$ in solution, Mg_2Si (black) and Fe-bearing skeletons unchanged; network partly destroyed.

FIG. 11.—AL-CU-Fe-MG ALLOY; 925-5BW 16. $\times 100$.

Ultimate strength 36,120 lb. per sq. in., Brinell hardness 99, elongation 0.7 per cent. Same as Fig. 9, but $CuAl_2$ is rounded and network much less noticeable.

tively identified as a precipitate; but in the alloys as cast and drawn at 800° F. a definite precipitation was visible at high magnification. In the

Al-Cu-Fe-Mg alloy, this precipitate was undoubtedly CuAl_2 (with possibly some Mg_2Si), even though some of the particles were not stained by the nitric acid quench, as in Fig. 22; in the Al-Cu-Ni-Mg alloy it



FIG. 12

FIG. 12.—AL-CU-NI-MG ALLOY, AS SAND-CAST. $\times 500$.
 NiAl_3 (light gray), T (dark gray) and Mg_2Si (black).



FIG. 13.

FIG. 13.—AL-CU-FE-MG ALLOY, AS SAND-CAST; NITRIC-ACID QUENCH, 8 SEC. $\times 1000$.
 CuAl_2 (black) and duplex particles of Fe-bearing constituents (FeAl_3 and X); no intragranular precipitate.



FIG. 14.

FIG. 14.—AL-CU-NI-MG ALLOY; C 600-25A; NITRIC-ACID QUENCH, 4 SEC. $\times 1000$.
 CuAl_2 (black) filigree and NiAl_3 (dark gray). Markings in matrix may be precipitate.



FIG. 15.

FIG. 15.—AL-CU-FE-MG ALLOY; C 600-25A. $\times 1000$.
 CuAl_2 (gray, massive areas) and duplex Fe-bearing particles and needles; matrix dotted with precipitate of CuAl_2 .

consisted probably of both NiAl_3 and CuAl_2 and possibly of some Mg_2Si . The particles were so small that polishing alone served to blacken them in part, and what assistance could be afforded by the use of etching reagents

was often thereby vitiated. (It is recommended that one-third of the specimen be etched in one reagent, the opposite third in another. This



FIG. 16.

FIG. 17.

FIG. 16.—AL-CU-NI-MG ALLOY; 950-5BW16; NITRIC-ACID QUENCH, 15 SEC. $\times 1000$. NiAl_3 (gray) and T (black) both mingled with NiAl_3 and as clumps or rounded particles; no intragranular precipitate.

FIG. 17.—AL-CU-Fe-MG ALLOY; 925-5BW16; NITRIC-ACID QUENCH, 15 SEC. $\times 1000$. CuAl_2 (black) and Fe-bearing needles; no intragranular precipitate.



FIG. 18.

FIG. 19.

FIG. 18.—AL-CU-NI-MG ALLOY; H T 600-25A. $\times 500$. NiAl_3 (light gray) closely associated with T , which in places occurs in clumps of small particles characteristic of heat treatment; Mg_2Si (black) and Fe-bearing skeletons at upper right.

FIG. 19.—AL-CU-NI-MG ALLOY; H T 600-25A. $\times 500$. NiAl_3 (light gray) passing into lamellar T . (dark gray).

procedure leaves an unetched band and a surface that can be studied from three angles.) These statements hold also for the specimens that were quenched and aged and then reheated.

Quenched and Aged Alloys

The alloys as simply quenched and aged are depicted in Figs. 10, 11, 16 and 17. The hardening of the Al-Cu-Ni-Mg alloy was marked by

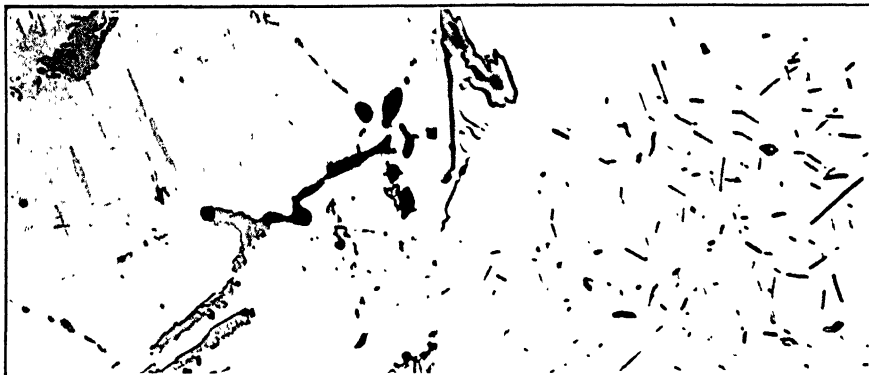


FIG. 20.

FIG. 21.

FIG. 20.—AL-CU-NI-MG ALLOY; H T 800-25A. $\times 500$.

T (large gray particles), Mg_2Si (black), and $NiAl_3$ (?) slivers.

FIG. 21.—AL-CU-NI-MG ALLOY; H T 800-25A; NITRIC-ACID QUENCH, 15 SEC. $\times 1000$.

Intragranular precipitate contains both etched ($CuAl_2$) and unetched ($NiAl_3$) particles.

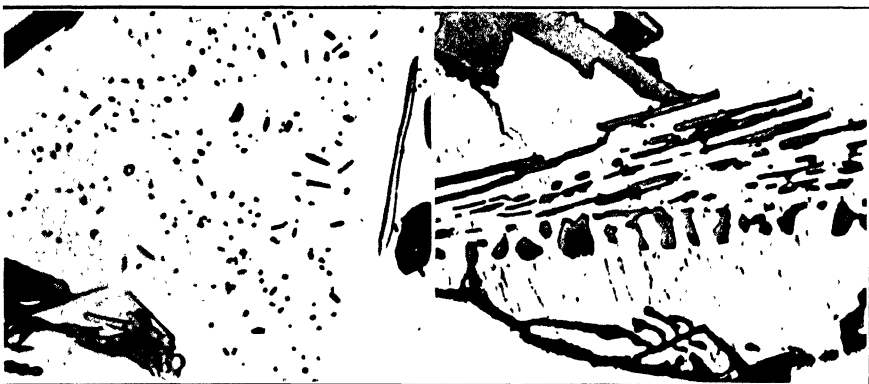


FIG. 22.

FIG. 23.

FIG. 22.—AL-CU-FE-MG ALLOY; H T 800-25A; NITRIC-ACID QUENCH, 15 SEC. $\times 1000$.

Fe-bearing skeletons and needle (gray) and $CuAl_2$ (black); some of precipitate unetched, though undoubtedly $CuAl_2$.

FIG. 23.—AL-CU-NI-MG ALLOY; C 500-50A; NITRIC-ACID QUENCH, 15 SEC. $\times 1000$. $NiAl_3$ (light gray), Mg_2Si (black), and matrix markings which may be intragranular precipitate.

some dissolution of the network through the absorption of all of the $CuAl_2$, some $NiAl_3$, and possibly of some *T*. The Mg_2Si and the iron-bearing

constituents apparently persisted unaltered. The characteristic structural feature of the quenched Al-Cu-Ni-Mg alloy was the clumps of small, globular particles of T (Figs. 16 and 18), nearly always associated with NiAl_3 . The Al-Cu-Fe-Mg alloy, however, was changed with respect to CuAl_2 , which in many places was rounded by partial solution, and to the network, which was somewhat broken up.

As cast, as quenched and aged, and in either of these conditions and reheated at 500° F., no intragranular precipitate was identified in the Al-Cu-Ni-Mg alloy, or in the Al-Cu-Fe-Mg alloy except as drawn at 500° F. for 50 hr. (Fig. 24). After etching, markings, such as are to be seen in Figs. 14 and 23, were developed in the specimens that were thought to have no precipitate, but these were interpreted to be etching

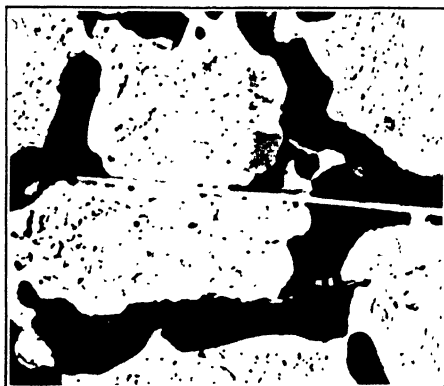


FIG. 24.—AL-CU-Fe-MG ALLOY; C 500-50A; NITRIC-ACID QUENCH, 30 SEC. $\times 1000$. I_2 (black) and Fe-bearing needles; intragranular precipitate of CuAl_2 .

effects. The appearance of some of these specimens before etching is illustrated in Figs. 13, 16, and 17.

When quenched and aged and then reheated at 600° F. for 25 hr. and air-cooled, the alloys did not differ materially in structure from their peculiarities as simply quenched and aged, except for the intragranular precipitate, which, in the Al-Cu-Ni-Mg alloy, was not absolutely distinct. Figs. 18 and 19 are typical of the Al-Cu-Ni-Mg alloy; and the latter metallograph portrays T formed from the reaction between NiAl_3 and liquid. The intragranular precipitate (of CuAl_2) was definitely present in the Al-Cu-Fe-Mg alloy.

The structure of both alloys as heat-treated and then drawn at 800° F. is much like that as heat-treated, from which it differs by the precipitate shown in Figs. 20, 21, and 22. This precipitate was acicular and globular in form. As has been indicated, the identification of the particles is difficult.

To judge from the metallography, and especially from the mechanical properties, of the alloys, this precipitation commences at approximately

500° F. (Table 3); but at this temperature the alloys must be soaked for 5 hr. or longer (Table 4) to accomplish it. It will be noted in this connection that the properties of either the cast or the heat-treated alloys after having been drawn at 400° F. for 25 hr. were about the same as those for the draw at 500° F. for 1 hr. As drawing at 300° F. for 25 hr. had nearly the same effect as drawing at 400° F. for 25 hr., it seems that precipitation does not occur from temperatures much below 500° F. In the case of the Al-Cu-Ni-Mg alloy, it was not possible to determine whether CuAl_2 and NiAl_3 were precipitated at different temperatures, because of the limitations of the etching media. It is likely that the hardening of the Al-Cu-Ni-Mg at 700° F. and of the Al-Cu-Fe-Mg at 800° F. is caused in part by the solution of this precipitate, whose state of division is strongly conducive to its absorption by the aluminum-rich matrix.

ACKNOWLEDGMENTS

Grateful acknowledgement is herewith extended to Lt. A. J. Lyon, Selfridge Field, Mt. Clemens, Mich., and the members of the Material Section, McCook Field, for their assistance in this investigation, and to Mr. S. D. Heron, of the Power Plant Section, McCook Field, for his kind criticism.

The Lead-antimony System and Hardening of Lead Alloys

BY R. S. DEAN,* LYALL ZICKRICK* AND F. C. NIX,* CHICAGO, ILL.

(New York Meeting, February, 1926)

THE first attempt to establish an equilibrium diagram of the lead-antimony series was made by Roland-Gosselin¹ in 1896. This investigation classified the system as a purely eutectiferous one, with the eutectic at 12.5 per cent. antimony and 228° C. In the next year, Stead² placed the eutectic temperature at 247° C. The error in temperature made by Roland-Gosselin, however, has been perpetuated in the literature with a remarkable degree of persistency; this value was accepted by Campbell (1902), and Ewen (1910),³ and will be found in the last edition of Desch's³ *Metallography* (1922). Gonterman's investigation, made in 1907, was the most complete one available at the time the present investigation was started. He concluded⁴ that the system was a simple eutectiferous one and placed the eutectic at 13 per cent. antimony and 247° C. Other investigations by Tammann (1907),⁵ Garbow (1909),⁶ Rudolfi (1910),⁷ Loebe (1911),⁸ and Leroux (1913)⁹ added little, if anything, to Gonterman's diagram.

A number of investigations have been made of physical properties of the alloys. The electrical conductivity of the series was studied by Matthiessen (1860)¹⁰ and by A. W. Smith (1921);¹¹ the thermoforce by Rudolfi (1910),¹² and Pelabon (1923);¹³ the specific heat by Durrer

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¹ Roland-Gosselin: *Bull. Soc. d'Encour.* [5] (1896) **1**, 1301.

² Stead: *Jnl. Soc. Chem. Ind.* (1897) **16**, 200.

³ Ewen *Jnl. Inst. Met.* (1910) **4**, 135; Desch: "Metallography." Longmans, London, 1922.

⁴ Gonterman: *Zeit. anorg. Chem.* (1907) **55**, 419.

⁵ Tammann: *Zeit. anorg. Chem.* (1907) **53**, 454.

⁶ Garbow: *Jnl. Russ. Phys. Chem. Soc.* (1909) **41**, 1241.

⁷ Rudolfi: *Zeit. anorg. Chem.* (1910) **67**, 85.

⁸ Loebe: *Metallurgie*, (1911) **8**, 7.

⁹ Leroux: *Comp. Rend.* (1913) **156**, 1764.

¹⁰ Matthiessen: *Pogg. Ann.* (1860) **110**, 28.

¹¹ Smith: *Jnl. Franklin Inst.* (1921) **192**, 101.

¹² *Op. cit.*

¹³ Pelabon: *Comp. rend.* (1923) **176**, 1305.

(1918),¹⁴ Muzzafar (1923),¹⁵ and Linnavouri (1923).¹⁶ The magnetic susceptibility was studied by Leroux (1913)¹⁷ and the electrical conductivity in the liquid state by Müller (1910);¹⁸ the thermal conductivity by Smith (1925).¹⁹ The mechanical properties have been studied by Ssaposchnikow (1907),²⁰ Ludwick (1916),²¹ Rosset (1905),²² Fairlee (1911),²³ and by Gurevitch and Hromatko (1921).²⁴

None of these investigations were made on alloys of which the past history was sufficiently known to make the values significant. This is shown by the present investigations, in which as much as 300 per cent. change in properties may be made by the heat treatment. We may, therefore, seriously question any evidence of constitution as determined from these physical properties.

Some observations indicating a change of properties in lead-antimony alloys with treatment are found in the literature. De Jussieu (1879)²⁵ made a study of alloys of near eutectic composition (type metals) and found that chill-cast alloys had a surface hardness. Dubosc (1905)²⁶ found that a change in properties was produced by quenching the alloys. It is not clear whether he carried his alloys into the partly liquid range or not, but Guillet (1906)²⁷ in discussing Dubosc's work states that the increased hardness takes place only when the solidus is passed. Brownsdon (1921)²⁸ made a few observations on changes in hardness of lead-antimony alloys with time, as did Goebel (1922).²⁹ None of these investigations described any definite reproducible treatment giving a difference in properties.

LEAD-ANTIMONY EQUILIBRIUM DIAGRAM

As the basis of our study of the lead-antimony system, it was necessary to develop as complete and as accurate as possible an equilibrium diagram particularly for the lead-rich end. For a number of years, work

¹⁴ Durrer: *Physik Zeit.* (1918) **19**, 86.

¹⁵ Muzzafar: *Metal Ind.* (1923) **23**, 67.

¹⁶ Linnavouri: *Chem. Abs.* (1923) **17**, 1182.

¹⁷ *Op. cit.*

¹⁸ Müller: *Metallurgie* (1910) **7**, 730.

¹⁹ Personal communication (1925).

²⁰ Ssaposchnikow: *Jnl. Russ. Phys. Chem. Soc.* (1907) **39**, 901.

²¹ Ludwick: *Zeit. anorg. Chem.* (1916) 161.

²² Rosset: *Centralblatt für Accumulatoren* (1905) **6**, 259.

²³ Fairlee: *Metal Ind.* (1911) **3**, 74.

²⁴ Gurevitch and Hromatko: *Chem. & Met. Engng.* (1921) **25**, 62.

²⁵ De Jussieu: *Ann. de Chim. et Phys.* [5] (1879) **18**, 138.

²⁶ Dubosc: Joint meeting of French and Belgian members of International Association for Testing Materials of Construction. 1905.

²⁷ Guillet: "Etude Industrielle des Alliages," Dunod, Paris. 1906.

²⁸ Brownsdon: *Jnl. Inst. Met.* (1921) **26**, 397.

²⁹ Goebel: *Zeit. Metallk.* (1922) **14**, 358.

toward this end has been in progress in the Hawthorne laboratories. In 1923, a preliminary paper was published,³⁰ in which evidence was adduced that antimony was soluble in solid lead up to from 2 to 3 per cent. at the eutectic temperature. This conclusion was based on the results of differential heating curves and microscopic investigations which showed that after prolonged annealing the evidences of eutectic which appeared in the cast alloys disappeared in the 2 per cent. alloy but not in the 3 per cent. alloy.

Further investigations of this limit of solubility have since been made by means of both thermal analysis and study of other properties. The alloys employed for these studies were made from Doe Run lead, which is a desilverized southeastern Missouri lead made by the St. Joseph Lead Co. The sample used contained no determinable amount of impurities. The antimony used was W. C. C. brand and analyzed: sulfur, 0.107 per cent.; arsenic, 0.021 per cent.; other impurities, traces only.

The alloys were made by melting together lead and antimony in a graphite crucible maintained at as low a temperature as possible so as to prevent excessive oxidation. In most cases the alloys were analyzed but the variance between the synthetic composition and the analysis was rarely sufficient to introduce an appreciable error in the conclusions.

The results of further heating-curve studies on the alloys showed that after annealing for four weeks at 235° C. the solid solubility was 2.45 per cent. antimony. This value was arrived at after studying several series of alloys made independently and studied by different investigators in this laboratory (Fogler, Quinn, Graves). Table 1 gives a typical set of results (Quinn). It should be noted that the eutectic arrest after this long annealing occurs at a point 10° C. higher than that obtained on cooling curves. This is explained by the growth of the lead and antimony particles.³¹

TABLE 1

PER CENT. ANTIMONY BY WEIGHT	HEAT ABSORPTION IN TERMS OF GALVANOMETER DEFLECTION, MILLIMETERS
3.25	25
3.00	16
2.75	9
2.50	1

As a further check on the solid solubility of antimony in lead, and particularly to study the change in solubility with temperature, the electrical conductivities were studied at various temperatures.³² For this purpose the alloys extruded as wires 1.35 mm. in diameter and 1 m.

³⁰ R. S. Dean: The Lead-antimony System. *Jnl. Amer. Chem. Soc.* (1923) **45**, 1683.

³¹ Benedicks and Arpi: *Metallurgie* (1907) **4**, 416.

³² R. S. Dean, W. E. Hudson and M. F. Fogler: The Lead-antimony System II. *Ind. & Eng. Chemistry* (1925) **17**, 246.

in length were used for measurement. All the wires were mounted on one frame and immersed in an oil (Crisco) thermostat. This thermostat was heated and cooled several times and the resistance measured until the same value was obtained for a given temperature when approached from either direction. This was taken as representing equilibrium conditions. The resistances were measured on a Wheatstone bridge to 0.0001 ohm. The results are shown in Table 2.

TABLE 2

PER CENT. ANTI- MONY BY WEIGHT	M _{HOS} 20° C	M _{HOS} 100° C.	M _{HOS} 150° C	M _{HOS} 200° C.	M _{HOS} 238° C
0.00	6.712	5.208	4 537	3 903	3.593
0.44	6.408	5.053	4.386	3 852	3 521
0.96	6.180	4.902	4.275	3.678	3.375
1.36	6.116	4.829	4 218	3 566	3.277
1.87	6.090	4.810	4.208	3 564	3.201
2.27	6.098	4.809	4.182	3 562	3.201
2.87					3.142
3.26	6.109	4.831	4.193	3 539	3 125

The solubilities at various temperatures as determined by breaks in the conductivity curves are shown in Table 3.

TABLE 3

TEMPERATURE, DEGREES CENTIGRADE	ANTIMONY, PER CENT
20	0 80
100	01
150	15
200	36
238	05
Eutectic temperature (247° C.)	2.45 by thermal analysis

Subsequent measurements of conductivities on wires cooled at various rates from temperatures above 200° C. showed that the rate of change at temperatures of 100° C. and below was exceedingly slow so that, in these experiments, equilibrium was not reached. Therefore, in order to determine the actual solubility limit at temperatures below 100° C. it was found necessary to allow very long periods of time. The room temperature experiments have been under way some 200 days without equilibrium being reached. At 110° C. equilibrium is reached after about seven weeks. The curve for the conductivity of wires of varying antimony content, heated at 110° C., until constant when measured at 32° C., is shown in the curve, Fig. 1. These measurements were made by the potentiometer method in an oil thermostat held at a constant temperature of 32° C. The measurements were made on wires 87.60 cm. in length. Each wire was weighed and the resistance calcu-

lated in ohms per meter-gram. The conductivity was then calculated in terms of that of a pure lead wire of the same weight per meter. This method was adopted to avoid introducing the density of the alloys, which is not known with the same accuracy as the conductivity. It is obvious

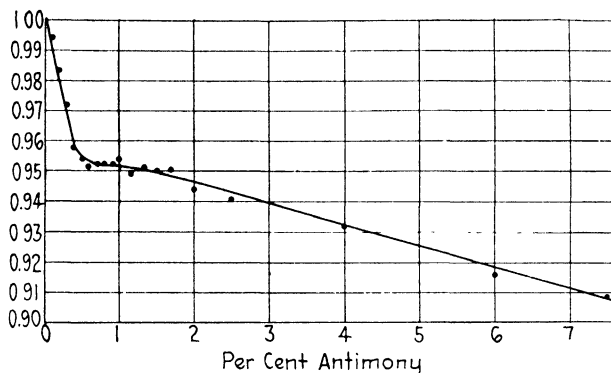


FIG. 1.—CONDUCTIVITY OF LEAD-ANTIMONY ALLOYS IN TERMS OF PURE LEAD, MEASURED AT 32° C. (THE CONDUCTIVITY OF PURE LEAD HAS BEEN TAKEN AS UNITY.) ALLOYS MADE FROM DOE RUN LEAD, ANNEALED FOR SEVEN WEEKS AT 110° C.

that the values given may be converted to specific conductivities by multiplying by

$$\frac{\text{Specific conductivity of lead} \times \text{density of alloy}}{\text{Density of lead}}$$

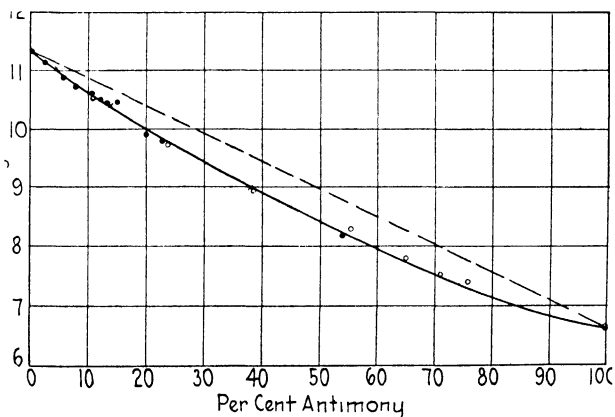


FIG. 1a.—DENSITY OF LEAD-ANTIMONY ALLOYS.

The curve, Fig. 1a, gives our data on density together with figures taken from the literature.

These results indicate that the equilibrium value of the solubility of antimony in lead at 110° C. is very near 0.5 per cent. antimony. In

these measurements a possible error has been introduced by measuring at 32° C. after heating at 110°. Since, however, the rate of change at either temperature is so slow, it is probable that no appreciable error takes place. An estimate of the solid solubility of antimony in lead at room temperature may be formed by extrapolating from the conductivities obtained after standing for varying periods at room temperature. This has been done graphically in Fig. 2, and gives a figure of approximately 0.5 per cent. antimony, indicating that the solubility at 110° C. should differ very little from that of equilibrium at room temperature. From the experiments, then, we conclude that equilibrium in the lead-antimony system is reached with extraordinary slowness at temperatures below 100° C.

The equilibrium in alloys above the solid-solution range has been only cursorily investigated by us. The investigations recorded in the literature have shown peculiarities in the system which might be interpreted

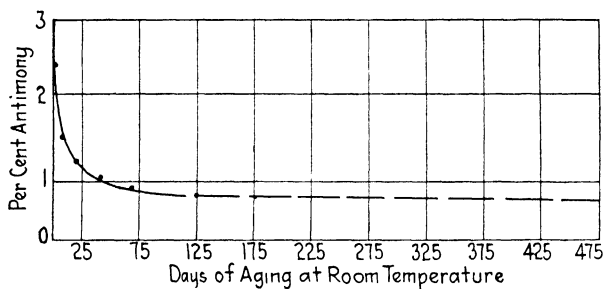


FIG. 2.—CHANGE OF PER CENT. ANTIMONY IN SOLUTION IN LEAD WHICH OCCURS ON AGING AT ROOM TEMPERATURE, AS INDICATED BY CONDUCTIVITY MEASUREMENTS.

as indicating a compound or compounds existing in the solid state. Among these peculiarities may be mentioned:

1. Apparent expansion of the 13 to 20 per cent. antimony alloys on freezing (use as type metal).
2. Different temperatures for eutectic on freezing and cooling (Gonterman, Dean).
3. Irregularities in the conductivity curve (Matthiessen).
4. Maximum in tensile strength curve near 10 per cent. (Fairlee, Gurevitch and Hromatko, and Rosset).

Since both lead and antimony contract on solidifying, an expansion of the 13 to 20 per cent. alloys would indicate a reaction taking place on solidification; it was, therefore, of interest to check this generally accepted expansion. This was done in a pyrex glass dilatometer using Crisco as the dilatometric medium. The technique involved no special features except the enclosure of the expansion tube in a steam jacket. The results are shown in Table 4 (M. F. Fogler).

TABLE 4

ANTIMONY-LEAD ALLOY PER CENT ANTIMONY	VOLUME OF ALLOY, c c	EXPANSION ON MELTING, c c.	EXPANSION, PER CENT.
0 (Pure Lead)		3.60*
10	107	2.45	2.31
12	105	2.42	2.47
16	114	2.35	2.06
100	1.45*

* Values for lead and antimony taken from Tammann: Textbook of Metallography.

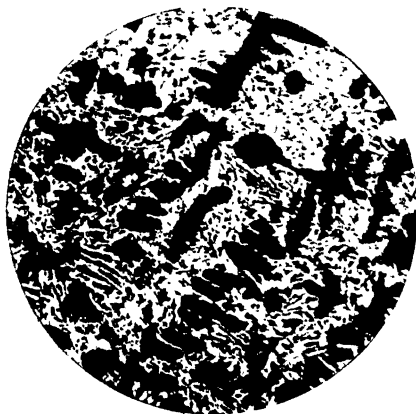


FIG. 3.—ANTIMONY 10 PER CENT. CAST. SOLID SOLUTION DARK, EUTECTIC LIGHT. $\times 100$.

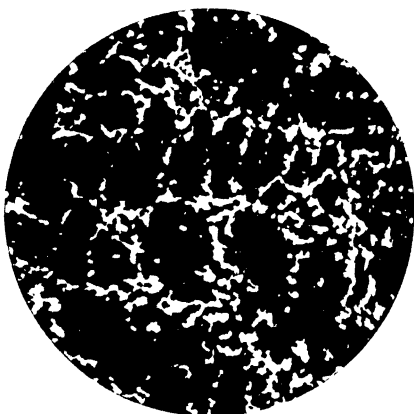


FIG. 4.—ANTIMONY 10 PER CENT. CAST AND ANNEALED 24 HR. AT 235°C . SOLID SOLUTION DARK, EUTECTIC LIGHT. $\times 100$.

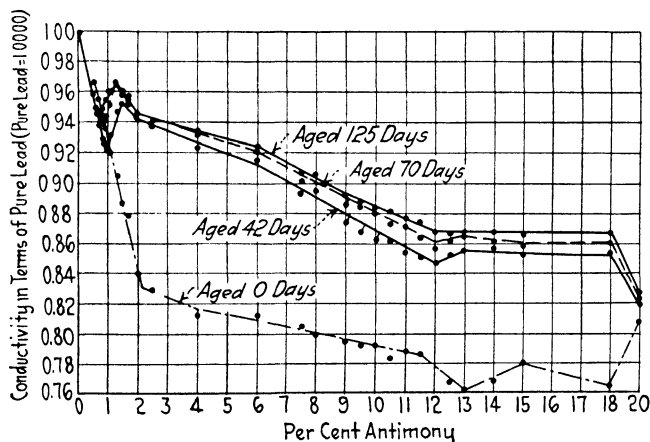


FIG. 5.—CONDUCTIVITY OF LEAD-ANTIMONY ALLOYS, ANNEALED AT 235°C ., QUENCHED IN WATER AT ROOM TEMPERATURE AND AGED VARYING PERIODS OF TIME AT ROOM TEMPERATURE.

The interpretation of these results is that the lead-antimony alloys of approximately eutectic composition behave normally with regard to

volume change on fusion and that the special properties of lead-antimony type metals should be attributed to some other factor.

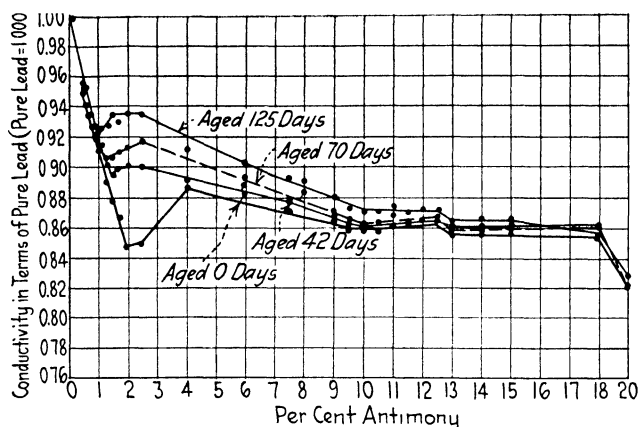


FIG. 6.—CONDUCTIVITY OF LEAD-ANTIMONY ALLOYS ANNEALED AT 235° C. AND COOLED SLOWLY. AGED VARYING PERIODS OF TIME AT ROOM TEMPERATURE.

The different eutectic temperatures observed on heating and cooling may be explained on the basis of agglomeration of the lead and antimony particles. The definite tendency toward this agglomeration is illustrated microscopically in Figs. 3 and 4.

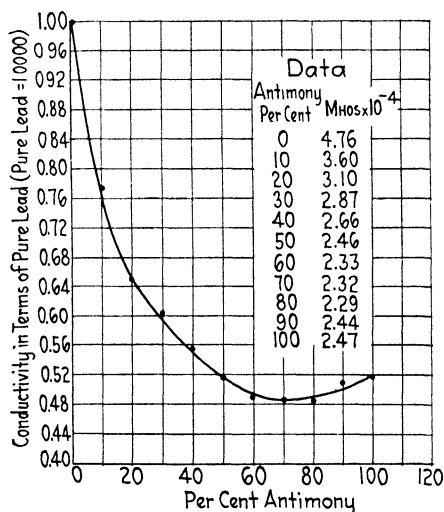


FIG. 7.—CONDUCTIVITY OF LEAD-ANTIMONY ALLOYS AS DETERMINED BY A. W. SMITH.

Previous determinations of conductivity have not taken into account the changes which take place in the conductivity of these alloys with treatment. In Figs. 5 and 6 are plotted in terms of pure lead the conduc-

tivity curves of lead-antimony alloy wires containing up to 20 per cent. antimony. These tests were made after the alloys had been aged for various periods of time at room temperature. They do not indicate a compound up to this composition. The most recent determination of the conductivities of the complete series of lead-antimony alloys has been made by A. W. Smith (1925). His results are shown in Fig. 7 and do not indicate a compound.

The tensile strength of cast lead-antimony alloys has been measured by Gurevitch and Hromatko, by Fairlee and by Rosset. All of these investigators find a maximum of tensile strength near 10 per cent. antimony. Measurements on extruded and annealed wires do not show any such maximum. Table 5 shows the tensile strength in kg. per sq. mm. of wires after heating for a period of seven weeks at 110° C.

TABLE 5

ANTIMONY, PER CENT	TENSILE STRENGTH KG. PER SQ. MM.
0.0	48
0.1	48
0.2	54
0.3	54
0.4	75
0.5	95
0.6	95
0.7	2.08
0.8	2.22
0.9	2.35
1.0	2.28
1.1	2.55
1.3	2.68
1.5	2.75
1.7	88
2.0	88
2.5	2.88
4.0	2.82
6.0	2.55
7.5	2.68
8.0	2.82
9.0	2.82
9.5	88
10.0	.94
10.5	94
11.0	94
11.5	3.07
12.0	2.94
12.5	2.94
13.0	3.00
14.0	3.00
15.0	2.94
18.0	3.00
20.0	3.00

It appears probable, therefore, that the tensile strength maximum in cast alloys is a function of the crystalline arrangement and has no signif-

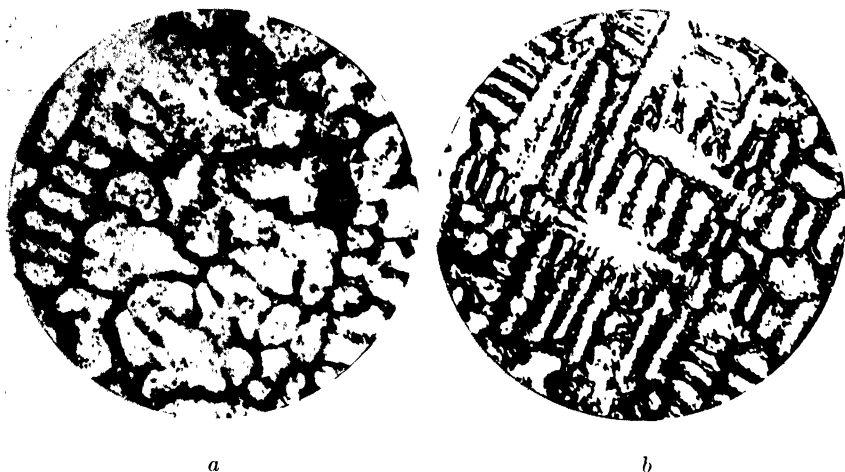


FIG. 8.—*a*. ANTIMONY-LEAD 2 PER CENT. CAST. *b*. ANTIMONY-LEAD 4 PER CENT. CAST. SOLID SOLUTION LIGHT, EUTECTIC DARK. $\times 100$.

icance so far as the equilibrium diagram is concerned. Also that the evidence adduced for the existence of a compound in this system is capable of other interpretation.

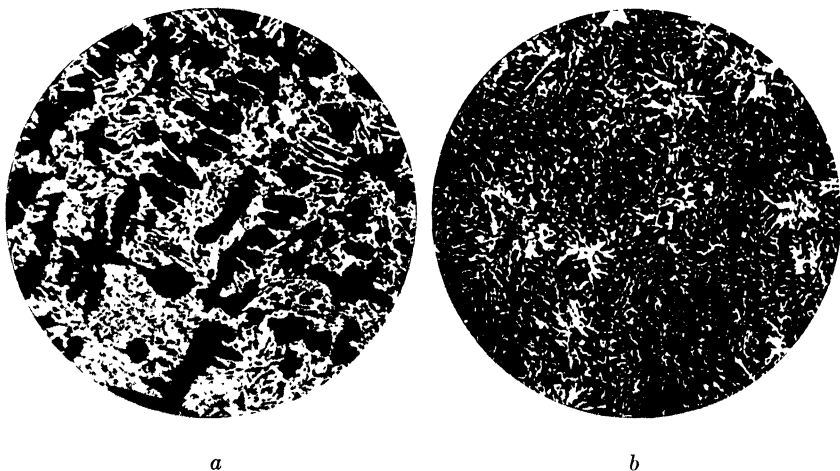


FIG. 9.—*a*. ANTIMONY-LEAD 10 PER CENT. CAST. $\times 100$. *b*. ANTIMONY-LEAD 13 PER CENT. CAST. $\times 100$.

A metallographic examination of the alloys did not reveal any unexpected features, but for purposes of record a series of photomicrographs

are included in this report, Figs. 8-11. The alloys above 2 per cent. cannot be satisfactorily etched with the acetic acid-hydrogen peroxide

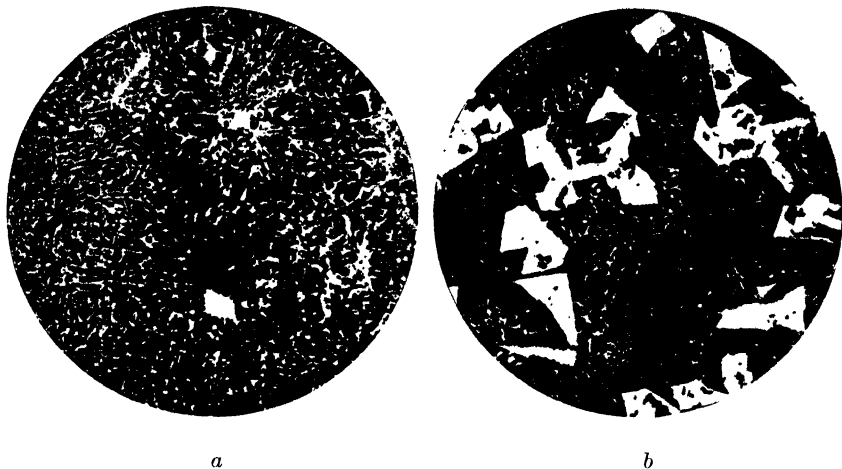


FIG. 10.—*a*. ANTIMONY-LEAD 15 PER CENT. CAST. $\times 100$. *b*. ANTIMONY-LEAD 20 PER CENT. CAST. $\times 100$.

etch developed in this laboratory for cable sheath.^{32a} The most satisfactory etch found for these higher alloys was an electrolytic one using perchloric acid as the electrolyte. These alloys in the cast state have

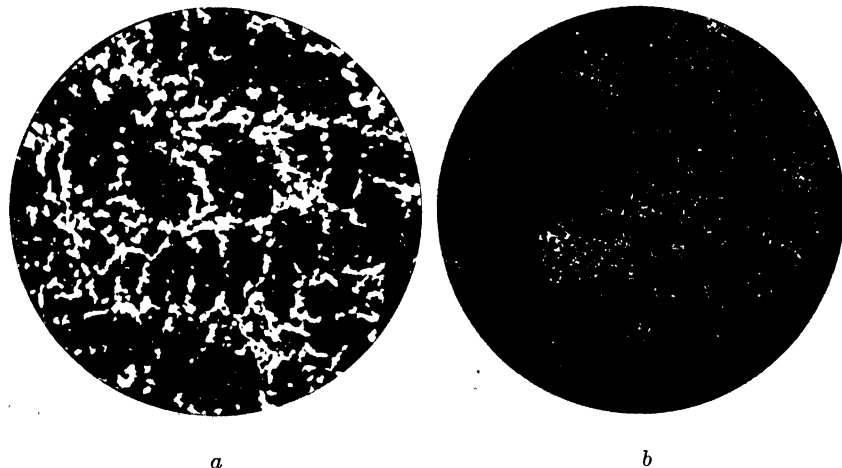


FIG. 11.—*a*. ANTIMONY-LEAD 10 PER CENT. ANNEALED 24 HR. AT 235° C. $\times 100$. *b*. ANTIMONY-LEAD 2 PER CENT. ANNEALED AT 235° C. $\times 100$.

the appearance of a simple eutectiferous system. Below 13 per cent. antimony, dendrites of solid solution appear in the ground mass. In

^{32a} Described by Rutherford: Am. Soc. Testing Mats. (1922.) **24**, 739.

the eutectic composition (Fig. 9b) small amounts of lead-rich and antimony-rich constituents appear as primary formed crystals. This is probably due to the alternate supersaturation of the melt with antimony and lead.

By annealing, a different structure is obtained. Two of these alloys are shown in Fig. 11. In the alloys below 2.5 per cent. the antimony apparently dissolves in the lead, giving a one-constituent alloy, and so far as this investigation was carried no metallographic evidence of the separation of the antimony constituent on cooling was found. In the higher antimony alloys the eutectic apparently breaks down into larger

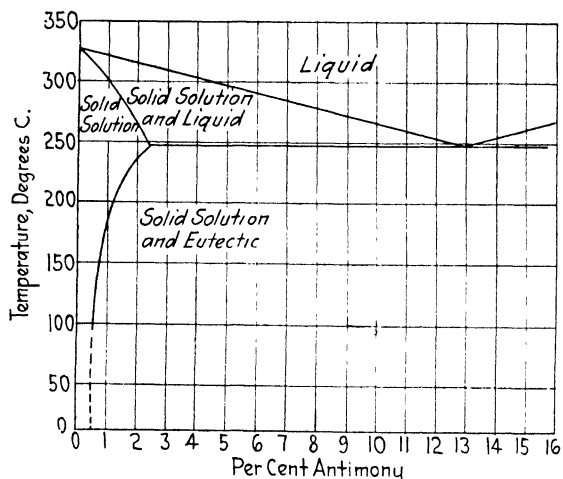


FIG. 12.—PARTIAL EQUILIBRIUM DIAGRAM OF THE SYSTEM LEAD-ANTIMONY.

crystals of lead and antimony. These results are summarized in Fig. 12, in the form of an equilibrium diagram.

AGE HARDENING IN LEAD-ANTIMONY SYSTEM

In March, 1923, it was discovered by R. S. Dean and W. E. Hudson that lead-antimony alloys, if heated above 200° and quenched, would show age-hardening phenomena. With the lead-antimony equilibrium diagram as given in the preceding section at hand, one could predict from the theory of hardening advanced by Merica (1919)³³ that such a hardening would take place in the lead-antimony alloys. According to this theory, the hardening is due to the separation of a constituent in a very fine state of subdivision, this constituent being more soluble at the temperature from which it is quenched than at the aging temperature.

Since it appeared that this age hardening might be of considerable commercial importance, it has been investigated in some detail. This phase of the investigation is still under way. A preliminary report of

³³ Merica, Waltenberg and Scott: *Trans. A. I. M. E.* (1920) **64**, 341.

the age-hardening effect was made in the paper by Dean, Hudson, and Fogler.³⁴ The following paragraph and table are quoted from that paper to give an indication of the general nature and magnitude of the phenomenon.

"In order to determine what alloys are susceptible to this hardening and at what composition the maximum hardening occurred, the alloy wires used in the conductivity experiments were heated from 238° to 243° for a period of several hours, quenched in water and aged 24 hr. at room temperature.

TABLE 6

PER CENT ANTIMONY	TENSILE STRENGTH, LB PER SQ. IN. $\times 10^{-3}$	
	IMMEDIATELY AFTER QUENCH	24 HR. LATER
0.44	2.68	2.70
0.96	2.75	3.10
1.36	3.20	4.00
1.87	4.05	9.03
2.27	4.65	10.18
2.87	5.33	8.88
3.26	5.58	6.68

It will be noted that the age hardening becomes detectable only after this period of aging in alloys containing more than 0.8 per cent. antimony.

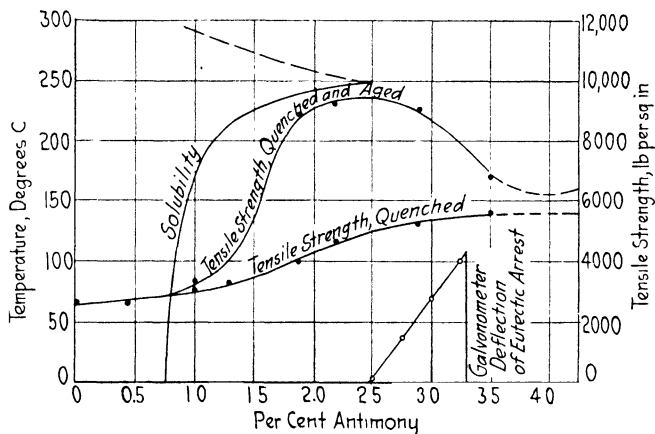


FIG. 13.—DIAGRAM SHOWING DISTINCT MAXIMUM IN AGE-HARDENING OF LEAD-ANTIMONY ALLOYS NEAR 2.5 PER CENT. ANTIMONY.

This finding is in accord with the theory of the age hardening of duralumin as proposed by Merica, Waltenberg, and Scott.

It will also be noted from the curve, Fig. 13, that there is a distinct maximum in age hardening near 2.5 per cent. antimony. It will be seen from the data already given that this corresponds to the maximum solubility. This fact may be explained on the dispersion theory by assuming that in alloys containing more than 2.5 per cent. antimony some rela-

³⁴ *Op. cit.*

tively large primary crystals of the separating constituent will be present after quenching, which will serve as nuclei and prevent as complete a dispersion of the separating material as in the alloy which represents the maximum solid solubility of the series.

We have seen that the solubility drops over a very long period of time, eventually reaching 0.5 per cent. or less. We should accordingly expect to get some age hardening under proper conditions in alloys down to that percentage. Our investigations have demonstrated this to be the case, although the age hardening at these low antimony percentages is slight.

We will now turn to a detailed study of the various factors affecting the age hardening in these alloys.

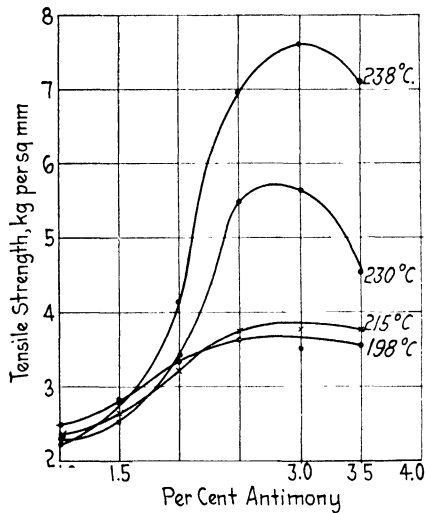


FIG. 14.—TENSILE STRENGTH OF LEAD-ANTIMONY ALLOYS ANNEALED AT TEMPERATURES INDICATED, QUENCHED, AND AGED FOR 24 HR. AT ROOM TEMPERATURE.

EFFECT OF HEATING TIME ON AGE HARDENING

Samples of lead-antimony alloy wires containing 2.5 per cent. antimony wire were annealed at 240° C. in a Crisco bath for various lengths of time and quenched in ice water. Table 7 gives the results for breaking strength after 24 hr. of aging at room temperature.

TIME OF ANNEALING	TABLE 7	
	BREAKING STRENGTH AFTER 24 HR., KG. PER SQ. MM.	ELONGATION, PER CENT. IN 8 IN.
30 min.	6.6	Brittle
10 min.	6.85	1.9
6 min.	6.7	2.0
3 min.	5.7	3.2
1 min.	4.3	10.0

These results indicate that heating beyond the time necessary to get all the antimony into solution has practically no effect on the tensile strength but increases brittleness. This is probably due to grain growth of the lead matrix.

EFFECT OF TEMPERATURE OF ANNEALING ON AGE HARDENING

Samples of lead-antimony alloy wires were annealed at temperatures of 198°, 215°, 230°, and 238° C. for 45 min., quenched in water at 15° C. and allowed to age 24 hr. at room temperature. Table 8 and Fig. 14 give the results:

TABLE 8

Wt Per Cent Sb	Temp of Anneal							
	238° C		230° C.		215° C.		198° C	
	Tensile Strength, Kg per Sq Mm	Per Cent Elong in 8 In	Tensile Strength, Kg per Sq Mm	Per Cent Elong in 8 In	Tensile Strength, Kg per Sq Mm.	Per Cent Elong in 8 In	Tensile Strength, Kg per Sq Mm	Per Cent Elong in 8 In
1	2 22		2 28	10 0	2 35	12 0	2 48	15 0
1 5	2 76		2 55	7 6	2 62	9 6	2 82	14 2
2 0	4 16		3 42	4 6	3 22	10 5	3 36	16 0
2 5	6 95		5 5	2 0	3 76	11 3	3 62	16 0
3 0	7 60		5 65	2 7	3 70	12 0	3 50	15.9
3 5	7 1		4 56	5 8	3 76	12 5	3 55	16 5

Each figure is the average of at least three values. These results indicate that to get hardening effects near the maximum, it is necessary to heat above 230° C. Since we have seen that the best results are obtained by using a heating temperature of 238° to 240°, this temperature has been used in the following experiments.

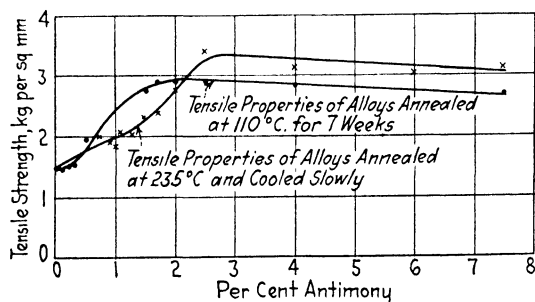


FIG. 15.—TENSILE PROPERTIES OF ALLOYS ANNEALED AT 235° C. AND COOLED SLOWLY, AND OF ALLOYS ANNEALED AT 110° C. FOR SEVEN WEEKS.

RATE OF HARDENING

In the preliminary study of these alloys, we made the assumption that since the tensile properties of a slowly cooled alloy were similar to

those of an alloy which had been quenched, aged, and softened by reheating to slightly above 100°C . for a period of time, the distribution of the antimony in the alloy was of the same order. Experiments on conductivity, however, showed that this was not the case. (See Figs. 15 and 16.)

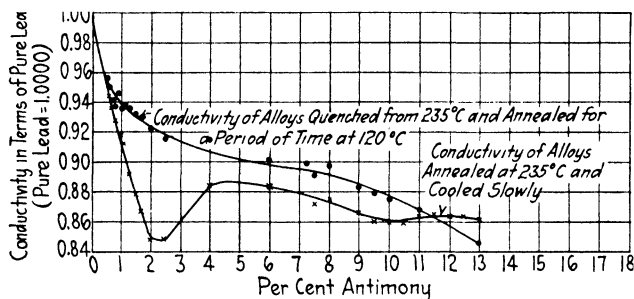


FIG. 16.—CONDUCTIVITY OF ALLOYS ANNEALED AT 235°C . AND COOLED SLOWLY, AND OF ALLOYS QUENCHED FROM 235°C . AND ANNEALED FOR A PERIOD OF TIME AT 120°C .

The slowly cooled alloy retained practically as much antimony in solid solution as the quenched alloy but separated it at a much slower rate (Figs. 17 and 18) and hence hardened very much more slowly (Figs. 19 and 20).

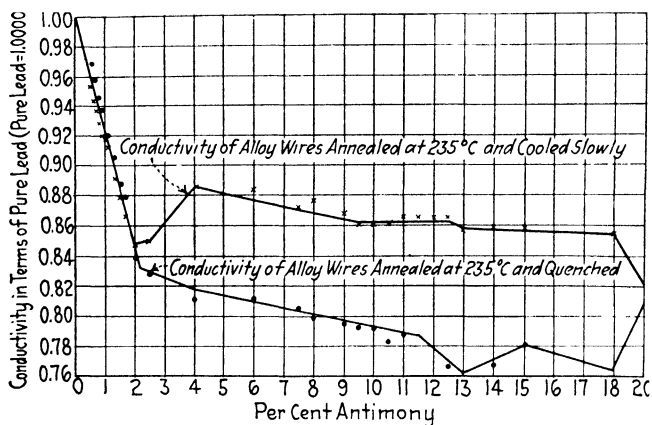


FIG. 17.—CONDUCTIVITY OF ALLOY WIRES ANNEALED AT 235°C . AND COOLED SLOWLY, AND OF ALLOY WIRES ANNEALED AT 235°C . AND QUENCHED. MEASUREMENTS TAKEN ON THESE ALLOYS BEFORE AGING.

The plots of per cent. antimony against conductivity, with the exception of the one immediately after quenching, exhibit an interesting phenomenon of passing through minima at the point where the curves change direction. (See Figs. 17 and 18.) The explanation of this is probably to be found in the autocatalytic nature of the breaking down

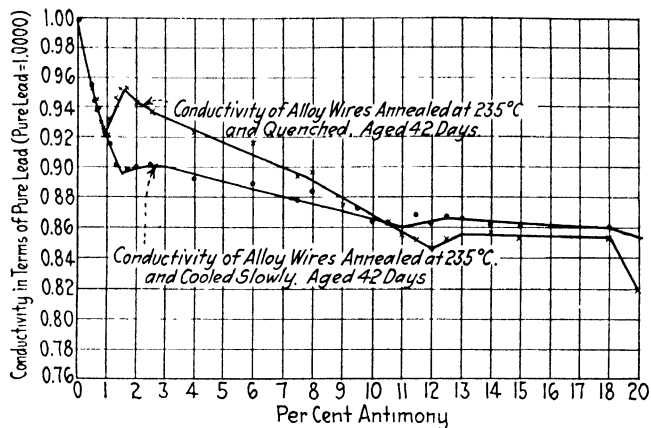


FIG. 18.—CONDUCTIVITY OF ALLOY WIRES ANNEALED AT 235° C. AND COOLED SLOWLY, AGED 42 DAYS, AND OF ALLOY WIRES ANNEALED AT 235° C. AND QUENCHED, AGED 42 DAYS.

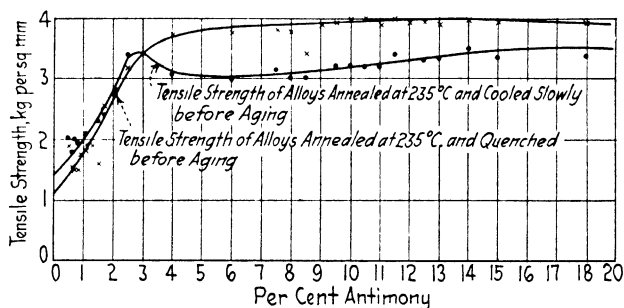


FIG. 19.—TENSILE STRENGTH OF ALLOYS ANNEALED AT 235° C. AND COOLED SLOWLY BEFORE AGING, AND OF ALLOYS ANNEALED AT 235° C. AND QUENCHED BEFORE AGING.

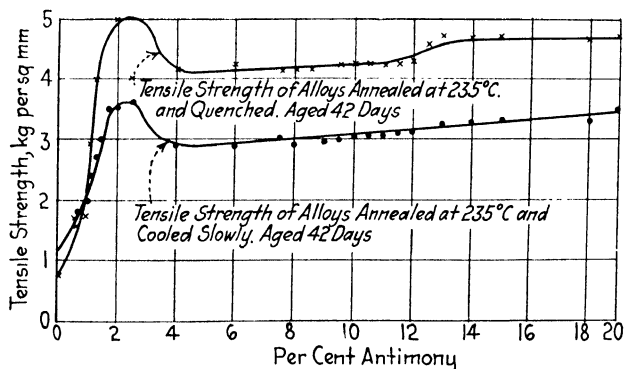


FIG. 20.—TENSILE STRENGTH OF ALLOYS ANNEALED AT 235° C. AND COOLED SLOWLY, AGED 42 DAYS, AND OF ALLOYS ANNEALED AT 235° C. AND QUENCHED, AGED 42 DAYS.

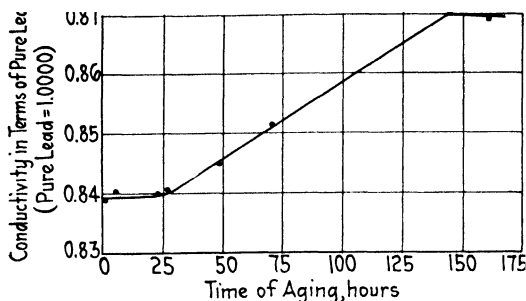


FIG. 21.—CONDUCTIVITY OF 1.5 PER CENT. ANTIMONY ALLOY ANNEALED AT 235° C., QUENCHED IN WATER AND AGED. MEASUREMENTS TAKEN AT 32° C.

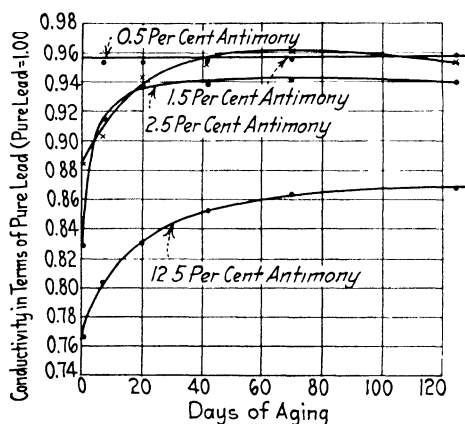


FIG. 22.—AGE HARDENING OF LEAD-ANTIMONY ALLOYS AT ROOM TEMPERATURE. CONDUCTIVITY IN TERMS OF PURE LEAD.

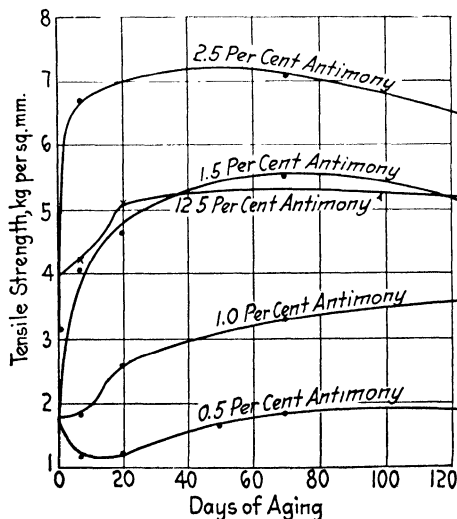


FIG. 23.—AGE HARDENING OF LEAD-ANTIMONY ALLOYS AT ROOM TEMPERATURE. TENSILE STRENGTH.

process. The alloys containing over 2.5 per cent. antimony have primary formed antimony crystals which serve as nuclei and therefore give increased rate of decomposition, which gives the minima in the curve immediately after slow cooling. Each further separation of antimony then accelerates the decomposition till a practically steady state is reached. The time conductivity curve therefore has three parts, a period of induction until for some reason nuclei are formed, a period of very rapid precipitation and a final very slow separation of the last portion. Such a curve for 1.5 per cent. antimony is shown in Fig. 21. An alternative explanation of these minima in conductivity is that the very finely divided condition of the disperse phase has a lower conductivity than the coarser dispersion which is formed a little later.

Effect of Antimony Content on Rate and Amount of Hardening

Tensile Strength.—In Fig. 22 is shown the change of conductivity with time of several alloys. We see that the 2.5 per cent. alloy breaks

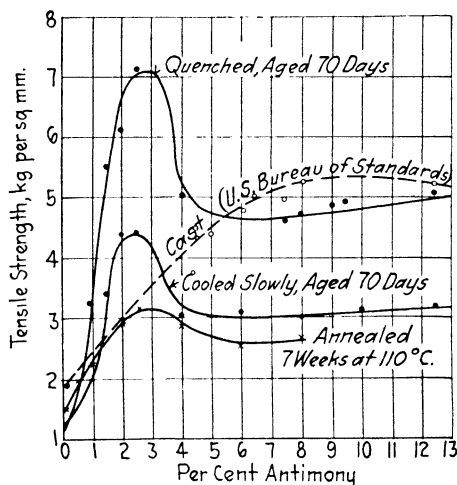


FIG. 24.—TENSILE PROPERTIES OF LEAD-ANTIMONY ALLOYS, HEAT TREATED AND CAST.

down the most rapidly and reaches the greatest hardness. In general, the rate seems to be proportional to the amount of antimony separating. In Fig. 23 the corresponding curves for tensile strength are shown.

In Fig. 24 is shown the maximum tensile strength reached by quenched and slowly-cooled alloys and alloys heated to 110° for five weeks. All these figures are for extruded alloys. The tensile strength of cast alloys from the figures of the Bureau of Standards (1923)³⁵ are also given for comparison. We have not studied the increase in tensile strength of cast alloys on heat treatment.

³⁵ Bur. of Stds. Circ. 101 (1924).

Brinell Hardness.—Lead-antimony alloys containing from 1 to 10 per cent. antimony were cast in small slugs 6 by $\frac{1}{2}$ by $\frac{1}{2}$ in. and rolled down to about $\frac{3}{8}$ -in. thickness. These strips were annealed at 238° C. for 15 min., quenched in cold water and allowed to age. The aging was followed by means of a Micro Brinell machine using a 2-kg. load on a $\frac{1}{16}$ -in. ball. Table 9 shows the Brinell numbers immediately after quenching and 11 days later. This shows that all of these alloys age harden, but there is a maximum at about 3 per cent. antimony.

TABLE 9		
Sb, PER CENT.	BRINELL NUMBER AFTER QUENCHING	BRINELL NUMBER 11 DAYS LATER
1	5 8	8.8
2	5 9	22 8
3	12 1	25 1
4	8 1	14 0
5	9 1	18 6
6	8 8	21 0
7	8 8	20 5
8	9 4	18.2
10	13 0	20 5

The change with time of the Brinell number of quenched rolled lead-antimony alloys is shown in Table 10 and Fig. 25. They all show

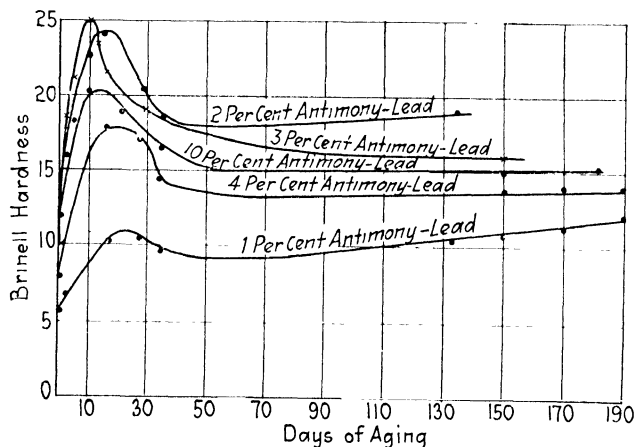


FIG. 25.—BRINELL HARDNESS OF LEAD-ANTIMONY ALLOYS ANNEALED AT 240° C., QUENCHED IN WATER AT ROOM TEMPERATURE, AND AGED.

a softening after the maximum is reached in about 16 days. They continue to soften until an equilibrium value is reached and then remain constant.

TABLE 10

Annealed	Antimony Content, Per Cent									
	1	2	3	4	5	6	7	8	10	
	Brinell Number									
	7 5	8 4	8 1	8 8	8 8	9 4	9 3	9 6	12 1	
Immediately after quenching	5 8	5 9	12.1	8 1	9.1	14 0	8.8	9.4	13.0	
4 hours after quenching	6 4	11 6	11 6	8 9	9 3	15 6	9.3	9.6	12.1	
7 hours after quenching	6 8	14 0	10 2	9.1	10.4	15 6	10 2	11.1	13.3	
24 hours after quenching	6 4	15 4	13 7	11.6	11 3	18 6	10.9	10.4	15 1	
30 hours after quenching	6 9	16 0	16 7	11 3	11.9	21 1	10.9	10 2	12 1	
52 hours after quenching	6 9	17.8	18 6	12 4	12.7	21 1	12 7	13 6	14.7	
72 hours after quenching	6 9	16 7	17 1	11 6	13 3	18 2	14 4	13.0	13.3	
101 hours after quenching	6 8	15 4	18 2	11 6	13.7	16 7	14.0	14.3	12.7	
167 hours after quenching	7 0	18.2	21 1	13 0	15 4	20 3	16.7	18.2	13.0	
264 hours after quenching	8 8	22 8	25.1	14 0	18 6	21 0	20.5	18.2	20.5	
340 hours after quenching	8 8	22 8	23 5	13 3	17 8	21 6	18.6	19.0	16.3	
412 hours after quenching	10.5	24 2	21 6	17 8	17 8	25 1	19.5	22 8	19.0	
697 hours after quenching	10 4	20 5	19 0	17 1	17.8	19 0	18 2	19.0	19.0	
864 hours after quenching	9.8	18.6	19 0	14 3	17.1	19 0	18.2	18.2	16 3	
3192 hours after quenching	10.7	19.0	17.1	14.7	17 8		15.1	19.0	16.3	
3605 hours after quenching	10 9	19.0	16.0	13.7	18 6		18.2	18.2	15.1	
3964 hours after quenching	11.36	18.6	15.4	14.0	19 5		17.1	19.5	16.3	
4561 hours after quenching	12 1	19.0	15 4	14.0	17.8		16.3	19.0	15.4	
5230 hours after quenching	11 9	18 2	15 4	13.7	16.7		15.4	17.8	16.7	

Effect of Rate of Quench on Rate and Amount of Hardening

Restricting our study now to the 2.5 per cent. alloy, which shows the maximum hardening, further experiments were made on the effect of

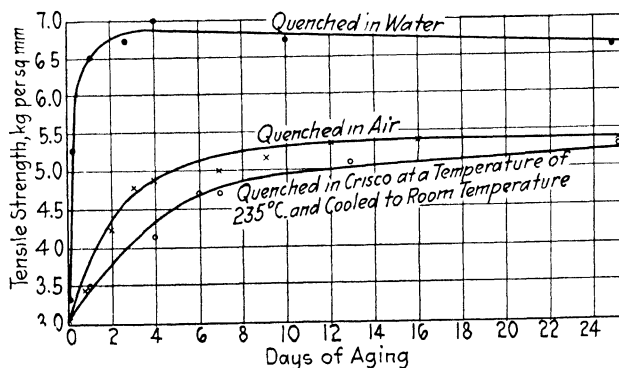


FIG. 26.—TENSILE STRENGTH OF 2.5 PER CENT. ANTIMONY ALLOY QUENCHED AT VARIOUS RATES AFTER ANNEALING AT 235° C., FOLLOWED BY AGING AT ROOM TEMPERATURE.

the rate of quench on the rate of hardening, using several quenching media. The results are shown in Fig. 26.

We see that both the rate of hardening and the final hardness reached are determined by the rate of quenching. This discovery is very important in the practical application of age hardening, since it allows us to reach a predetermined value of hardness and tensile strength in one operation rather than by the process of producing the maximum hardening and then softening by reheating. A study of the effect of the rate of quench on the possible combinations of tensile strength and elongation is shown in *A* of Fig. 27. Since all the points fall on a single smooth curve, the combination is the same regardless of the rate at which it is reached. The combinations on this curve are, however, better than those obtained by a reheating process as shown in *B* of Fig. 27. This poor elongation of the reheated alloys is probably due to crystal growth of the matrix.

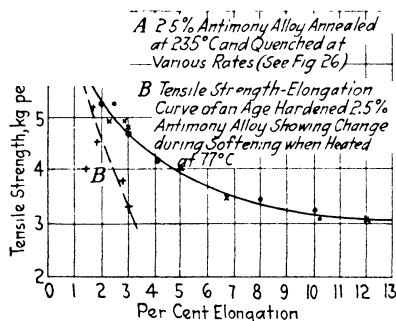


FIG. 27.—*A*. ANTIMONY ALLOY, 2.5 PER CENT. ANNEALED AT 235° C. AND QUENCHED AT VARIOUS RATES (SEE FIG. 26). *B*. TENSILE STRENGTH-ELONGATION CURVE OF AGE-HARDENED 2.5 PER CENT. ANTIMONY ALLOY SHOWING CHANGE DURING SOFTENING WHEN HEATED AT 77° C.

This effect of rate of quench on rate of hardening seems to offer an explanation of a paradoxical phenomenon in steel hardening which has recently received considerable attention,³⁶ viz.: Oil quenching gives more austenite (solid solution) than a more drastic water quench. It would appear that the explanation may not be in the amount of austenite retained immediately on passing through the critical range (solubility range) but in the rate at which the retained austenite breaks up after having passed from the critical range. From an analogy with the lead-antimony alloys, we would expect the oil-quenched material to break down more slowly, hence showing more austenite at room temperature.

SOFTENING OF LEAD-ANTIMONY ALLOYS AT ELEVATED TEMPERATURES

Lead-antimony alloy wires 1.37 mm. diameter containing 2.5 per cent. antimony were annealed at 238° C. for 15 min., quenched in cold

³⁶ Bain: Amer. Soc. Steel Treat. (1925) 8, 14; Mathews: H. M. Howe lecture. Trans. A. I. M. E. (1925) 71.

water and allowed to age at room temperature for 10 days. The breaking strength after that time was 10.1 kilos. These wires were placed in ovens at various temperatures and decrease in breaking strength followed from time to time. Table 11 gives the results (M. F. Fogler), which are plotted in Fig. 28. These indicate that, depending on quenching technique, there is, for any particular temperature, an equilibrium value for the breaking strength. That value in each case is indicated by the flattening of the curve. Table 12 gives the equilibrium values for the four temperatures studied.

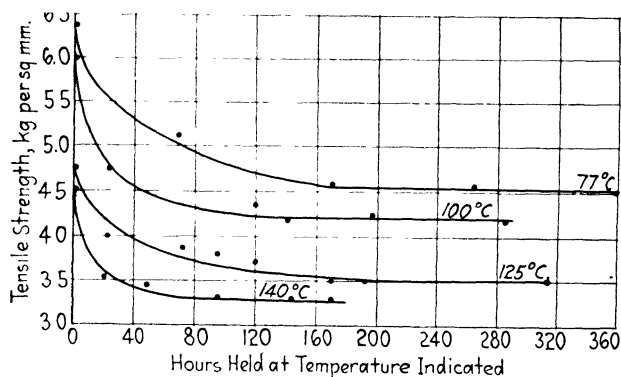


FIG 28.—DETERIORATION TESTS ON 2.5 PER CENT. ANTIMONY ALLOY.

TABLE 11

77° C		100° C		125° C		148° C	
Time, Hours	Breaking Strength, Kg per Sq Mm	Time, Hours	Breaking Strength, Kg per Sq Mm	Time, Hours	Breaking Strength, Kg per Sq Mm	Time, Hours	Breaking Strength, Kg per Sq. Mm
3 5	6 37	1	6 00	1	4 70	0 5	4.55
7	6 05	5	5 50	2	4 62	1	4 30
24	5 56	24	4 76	22	3 96	4	3 96
72	5 16	120	4 36	72	3 88	7	3 82
170	4 55	144	4 15	95	3 52	23	3 56
264	4 55	193	4 22	119	3 70	48	3 48
288	4 36	284	4 15	146	3 62	72	3 42
360	4 50			171	3 48	96	3 32
432	4 43			191	3 48	144	3.36
				262	3 62	168	3 36
				311	3 56		
				336	3 62		

TABLE 12

TEMPERATURE,
DEGREES CENTIGRADEBREAKING STRENGTH,
KG. PER SQ. MM.

77

100

125

148

3.60

3.36

These figures are plotted in Fig. 29 and an extrapolation to room temperature is made. This extrapolation indicates that for the quenching technique used, a breaking strength of about 5.25 kg. per sq. mm. may be considered the equilibrium value at 25° C. This is about 78 per cent. of the maximum noted strength and about twice that of the untreated wire. These results are interpreted as indicating that the age-hardening effect is stable. This is in agreement with Jeffries'³⁷ findings on duralumin (1924).

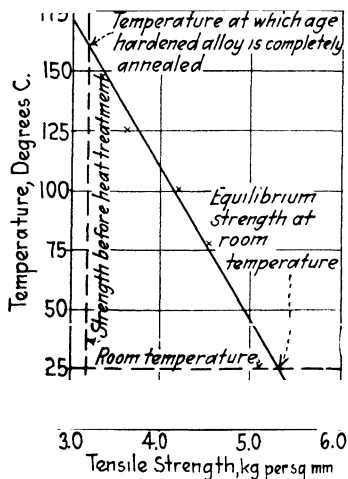


FIG. 29.

Microscopic Examination of Age-hardened Alloy

Due to the softness of the alloy, the ordinary methods of metallography do not show any change on age hardening. However, with a greatly improved technique developed by F. F. Lucas, in the Bell Telephone Laboratories, the decomposition of the solid solution may be followed microscopically.

SUMMARY

In previous papers the solid solubility of antimony in lead has been shown to vary from 2.45 per cent. at the eutectic temperature to less than 0.8 per cent. at room temperature. The discovery of a marked age-hardening phenomenon in lead-antimony alloys has also been reported and its connection with this solubility change discussed. It was also pointed out that the solid solutions below 1 per cent. were quite stable and broke down very slowly, making it difficult to determine the actual solubility at room temperature.

In the present paper evidence has been presented which shows that:

³⁷ Jeffries: *Trans. A. I. M. E.* (1924) **70**, 303.

1. The solid solubility of antimony in lead at room temperature is at least as low as 0.5 per cent. and probably not far from this figure.

2. The evidence which has been put forward for the existence of a compound in the lead-antimony system is capable of other interpretation.

3. The lead-antimony alloys of approximately eutectic composition behave normally with regard to volume change on solidification.

4. Age hardening may be observed in all lead-antimony alloys containing more than 0.5 per cent. antimony.

6. The rate and degree of age hardening is determined by the rate of cooling.

7. An equilibrium value for the strength of the alloy is reached at any given temperature. This value depends on the temperature and previous treatment of the alloy.

These data and a study of other factors affecting hardening in these alloys has given some new evidence on the mechanism of hardening in general and has suggested an explanation of some unusual phenomena observed in steel hardening.

ACKNOWLEDGMENT

This paper has necessarily been made up of work which has been in progress in these laboratories over a considerable period of time, and we wish to acknowledge the work of W. E. Hudson and M. F. Fogler, who were previously associated with the senior author in this work and whose notes have been freely drawn upon in making up this article. Our thanks are also due to W. A. Scheuch, in charge of metallurgical development and F. W. Willard, Assistant Superintendent of Development at the Western Electric Co., Inc., for their hearty cooperation in this work.

DISCUSSION

R. S. DEAN, L. ZICKRICK AND F. C. NIX ((written discussion).—With the development of a method for preparing metallographic specimens of lead-antimony alloys as suggested by F. F. Lucas¹ of the Bell Telephone Laboratories, Inc., it has been found possible to determine microscopically the lower limit of the solubility of antimony in lead, and also to explain the mechanism associated with the hardening process for these alloys.

This method consists of preparing the surfaces of the alloys for microscopic observation by cutting with a microtome instead of polishing, only a slight etch with acetic acid and hydrogen peroxide being necessary to develop the structure.

¹ See page 909.

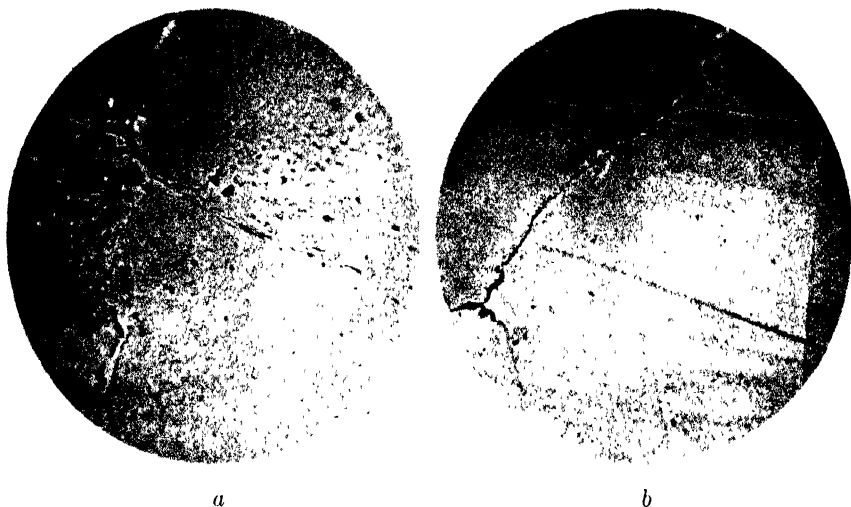


FIG. 30.—ANTIMONY, 0.50 PER CENT., QUENCHED IN WATER AT 10° FROM 235° C. AND AGED AT ROOM TEMPERATURE, $\times 500$. *a*, IMMEDIATELY AFTER QUENCH, BRINELL NUMBER 4.40; *b*, 24 HOURS LATER, BRINELL NUMBER 5.08.

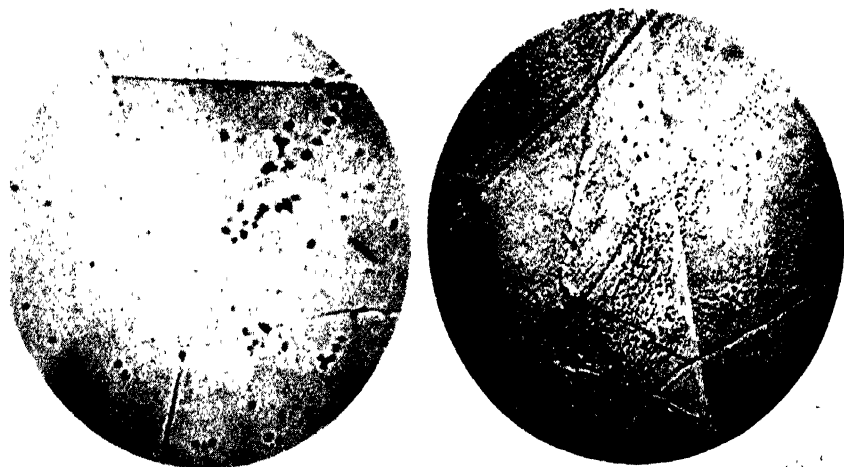


FIG. 30, CONT'D.—*c*, 10 DAYS LATER, BRINELL NUMBER 5.26; *d*, 1 MONTH LATER, BRINELL NUMBER 4.84.



FIG. 30, CONT'D.—*c*, REHEATED TO 110° C. FOR 1 WEEK, BRINELL NUMBER 4.84.

FIG. 31.—ANTIMONY, 1.0 PER CENT., QUENCHED IN WATER AT 10° FROM 235° C. AND AGED AT ROOM TEMPERATURE, $\times 500$
a, IMMEDIATELY AFTER QUENCH, BRINELL NUMBER 5.73.

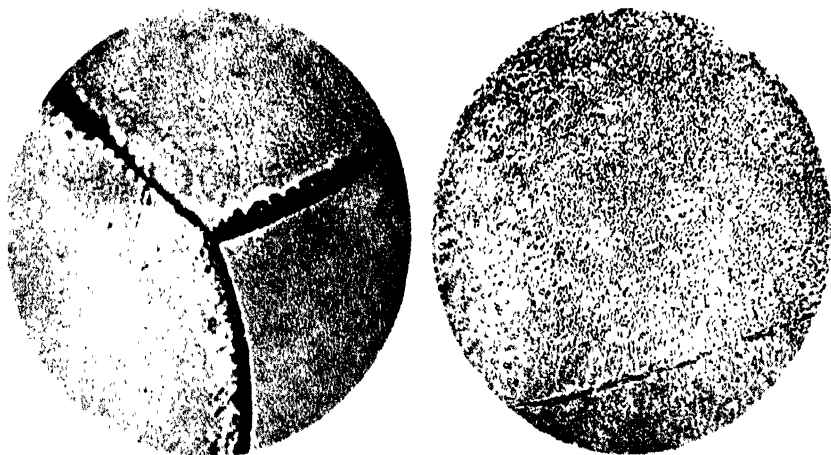


FIG. 31, CONT'D.—*b*, 24 HOURS LATER, BRINELL NUMBER 6.50; *c*, 10 DAYS LATER, BRINELL NUMBER 8.6.

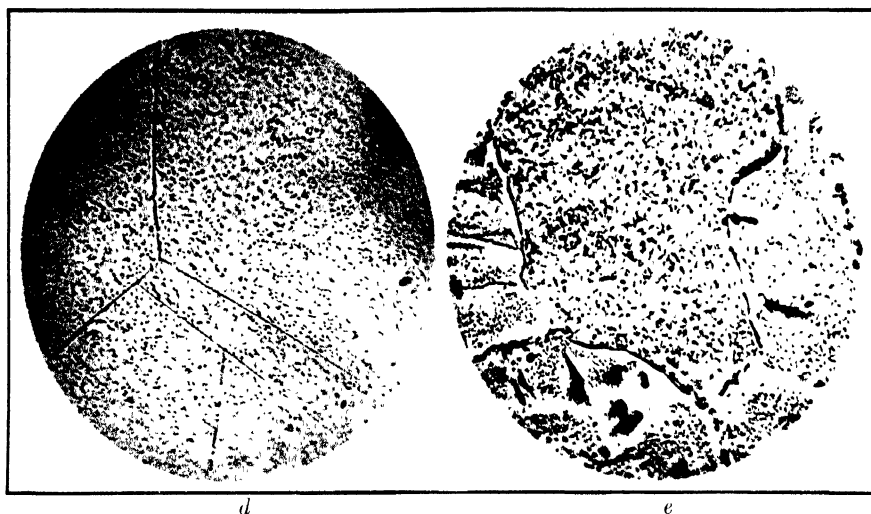


FIG. 31, CONT'D.—*d*, 1 MONTH LATER, BRINELL NUMBER 8.21; *e*, REHEATED TO 110°C . FOR 1 WEEK, BRINELL NUMBER 6.70.

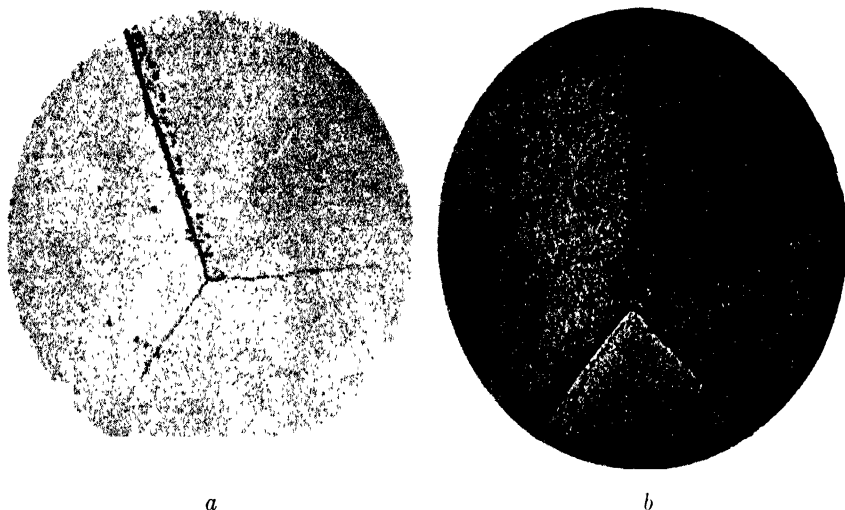


FIG. 32.—ANTIMONY, 2.0 PER CENT, QUENCHED IN WATER AT 10° FROM 235°C ., AGED AT ROOM TEMPERATURE, $\times 500$. *a*, IMMEDIATELY AFTER QUENCHING, BRINELL NUMBER 12.00; *b*, 24 HOURS LATER, BRINELL NUMBER 16.36.

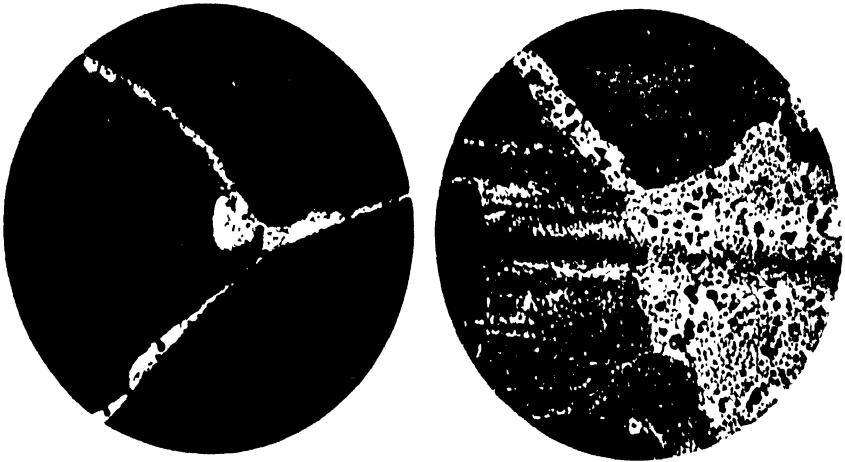


FIG. 32, CONT'D.—*c*, 10 DAYS LATER, BRINELL NUMBER 22.40; *d*, 1 MONTH LATER, BRINELL NUMBER 20.76.

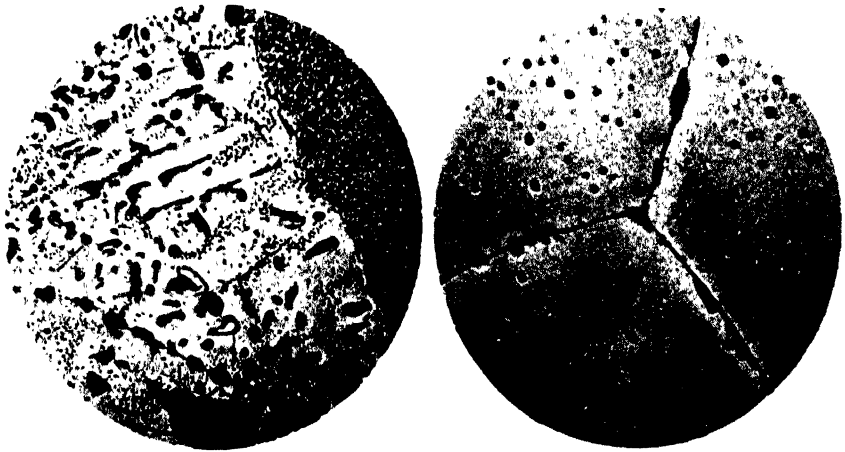


FIG. 32, CONT'D.—REHEATED TO 110° C. FOR 1 WEEK, BRINELL NUMBER 10.36.

FIG. 33.—ANTIMONY, 3.0 PER CENT., QUENCHED IN WATER AT 10° FROM 235° C., AGED AT ROOM TEMPERATURE, $\times 500$. *a*, IMMEDIATELY AFTER QUENCHING, BRINELL NUMBER 14.32.

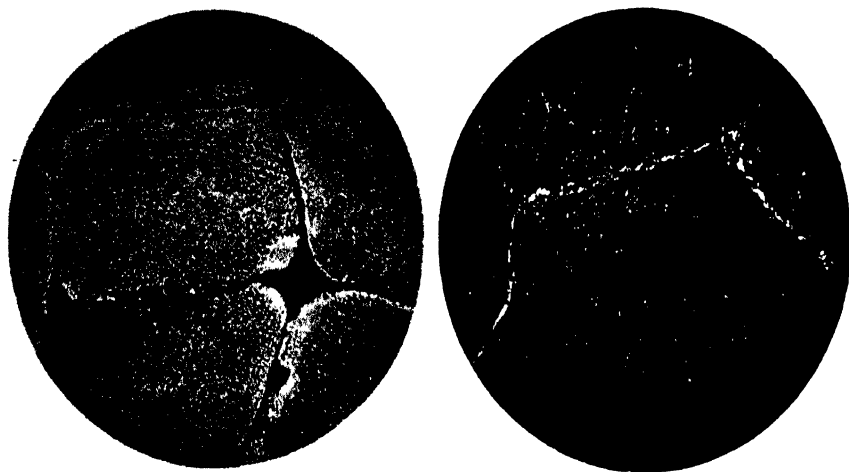


FIG. 33, CONT'D.—*b*, 24 HOURS LATER, BRINELL NUMBER 18.32; *c*, 10 DAYS LATER, BRINELL NUMBER 25.08.

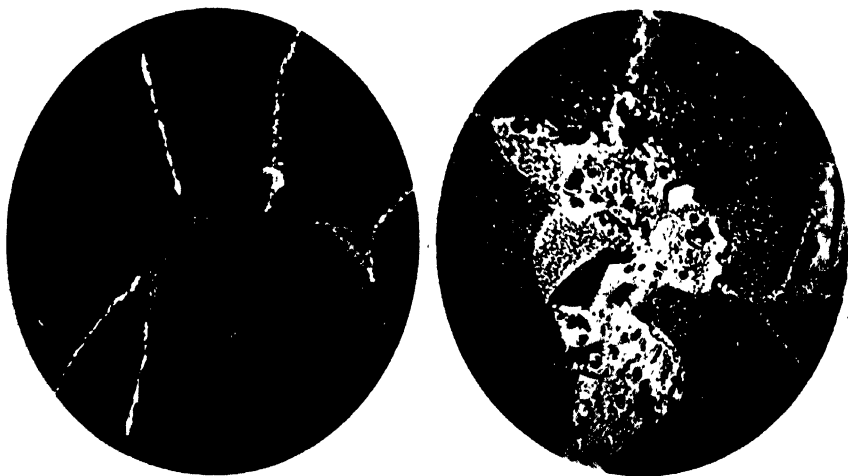


FIG. 33, CONT'D.—*d*, 1 MONTH LATER, BRINELL NUMBER 20.24; *e*, REHEATED TO 110° C. FOR 1 WEEK, BRINELL NUMBER 11.16.

MECHANISM OF DISPERSION HARDENING

Studies of the physical properties have indicated that the hardening of lead-antimony alloys is associated with a breaking down of the lead-antimony solid solution into a highly-dispersed antimony-rich constituent in the ground mass.

For a metallographic study of this phenomenon, alloys of pure Doe Run lead with 0.5, 1.0, 2 and 3 per cent. of Chinese antimony were cast, rolled and after annealing at 235° C., quenched in water at room temperature. These compositions were selected so that the range of solid solubility might be covered and in addition, an alloy studied which would show primary antimony after quenching from a temperature of 235° C.

After preparing the specimens, they were examined under the microscope and photographed at 500 diameters. The results are shown in Figs. 30 to 33. It will be seen that after aging 24 hrs., all except the 0.5 per cent. alloy show a distinct breaking down within the crystals. A study of these alloys after 10 days shows a still further breaking down. A considerable number of observations have shown that this breaking down apparently starts at the grain boundaries. In the case of 2 and 3 per cent. alloys after aging 10 days, it will be seen that the crystal boundaries appear lighter in color than the main body of the crystal. There is good reason to believe that these large patches occurring in the widened grain boundary are agglomerated antimony which has formed from smaller particles of antimony that first separate. The light color of the grain boundary is due then, to the lesser degree of dispersion of its antimony content as compared to the surrounding crystals. The samples observed after aging one month show further progress of this agglomeration process, it being particularly noticeable in the 2 per cent. alloy. It will be noted, however, that no breaking down appears in the 0.5 per cent. alloy.

To obtain further information in the breaking-down process of these alloys, they were reheated to 110° C. for one week. This resulted, as will be seen in the photomicrographs, Figs. 30 to 33, in a considerable increase in the size of the antimony particles, and therefore, an increased area which appears light under the microscope. The 0.5 per cent. alloy does not, however, show any signs of breaking down, indicating that it is also stable under conditions of reheating to 110° C.

The writers wish to thank E. F. Salchow and L. G. Swenson, to whom credit is due for the metallographic work.

W. B. PRICE, Waterbury, Conn.—Do you find any difference in the kind of lead you use? Do small impurities, such as nickel, copper, or anything of that type, affect the limit of solubility?

R. S. DEAN.—It does have an effect. We are not prepared to say just quantitatively what these effects are, but copper apparently increases the

solid solubility somewhat. We are working on that, but I would not want to make a definite statement at this time.

C. R. HAYWARD, Cambridge, Mass. (written discussion).—In connection with the results of age hardening of lead-antimony alloys presented by Dean, Zickrick and Nix some tests made on a lead-antimony-tin alloy may be of interest. These were made by J. P. Ramsey, Jr., working under the writer's direction in the laboratories of the Massachusetts Institute of Technology. The alloy used was a type metal made up to contain 94 Pb, 3 Sb and 3 Sn, but not subsequently analyzed to get the exact final composition.

A sheet of this metal, about $\frac{1}{4}$ in. in thickness, was poured in an iron mold and cut into squares. These were aged for 2 weeks during which time hardness tests were taken periodically. Some of the specimens after aging for $2\frac{1}{2}$ days at room temperature were reheated to various temperatures, quenched in water, and reaged for 6 days. Another lot was similarly treated after aging for 6 days. Some of the specimens were also subjected to the Erichsen test. The results are shown in the following tables and curves.

TABLE 1.—*Results of Aging Cast Metal*

Time after Casting	Brinell Hardness	Erichsen Test
30 min.	12.4	145
90 min.	13.3	142
3 hr.	14 1	132
4½ hr.	14 3	123
24½ hr.	14.7	114
48 hr.	15.0	112
54 hr.	15 3	
6 days	16 5	
14 days	16 5	

The figures in Table 1 are plotted in Figs. 34 and 35.

TABLE 2.—*Results of Reheating and Reaging Metal 2½ Days after Casting*

Temperature to Which Heated, Deg. C	Brinell Hardness					
	Before Heating	Time of Aging after Heating				
		1 Hr.	2 Days	4 Days	5 Days	6 Days
146	15 3	14 5	14 0	14 8	15 3	14.2 (?)
155	15 3	13 7	11.9	13 0	13.5	14 2
170	15.3	12 8	12 8	12 8	13.7	13 7
185	14.8	12.4	12.4	12 8	13 3	14 0
200	14.8	12.4	13.3	13.3	15 9	16.5
218	14.8	12 8	17.0	19.3	19.3	19.3
235	14.5	13.3	21.0	21.8	23.3	23.8

The figures from Table 2 giving the effect of aging for six days are plotted in Fig. 3.

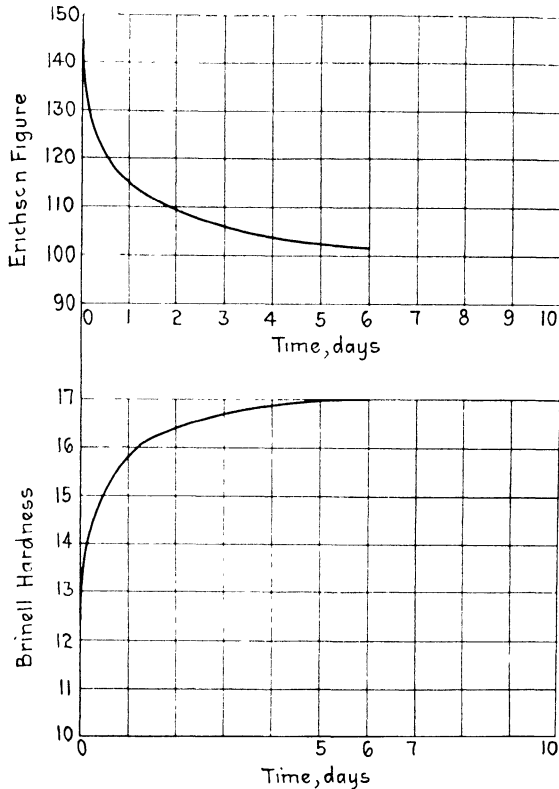


FIG. 34.—AGING OF METAL AS SHOWN BY ERICHSEN TEST AND BY BRINELL TEST.

TABLE 3.—Results of Reheating and Reaging Metal 6 Days after Casting

Temperature to Which Heated, Deg. C.	Before Heating	Brinell Hardness						
		Time of Aging after Heating						
		5 Min	1 Hr.	1 Day	2 Days	3 Days	8 Days	11 Days
132	16.5	15.9	...	15.9	15.9	15.9	15.3	15.3
156	16.5	14.8	14.5	14.2	13.5	13.5	14.2	13.7
216	16.5	13.7	...	16.5	17.2	17.8	20.1	19.3
237	16.5	13.7	15.0	20.1	20.9	22.8	22.8	24.5

Several facts are brought out by the figures in Tables 2 and 3 and Figs. 1 and 2:

1. Reheating the cast metal after it has stood $2\frac{1}{2}$ days causes softening which increases with the temperature from 130 to 210°C .

2. If the metal is reheated to above 200° C. and quenched in water a marked softening takes place but age hardening begins at once. The speed and extent of the hardening increases with the temperature of the annealing.

3. After annealing between 170 and 200° C., and quenching in water the softening effect is almost as great as at higher temperatures but age hardening does not set in for several days and then progresses slowly.

4. After annealing between 140 and 170° C., and quenching in water the metal continues to soften for several days and then commences to age very slowly.

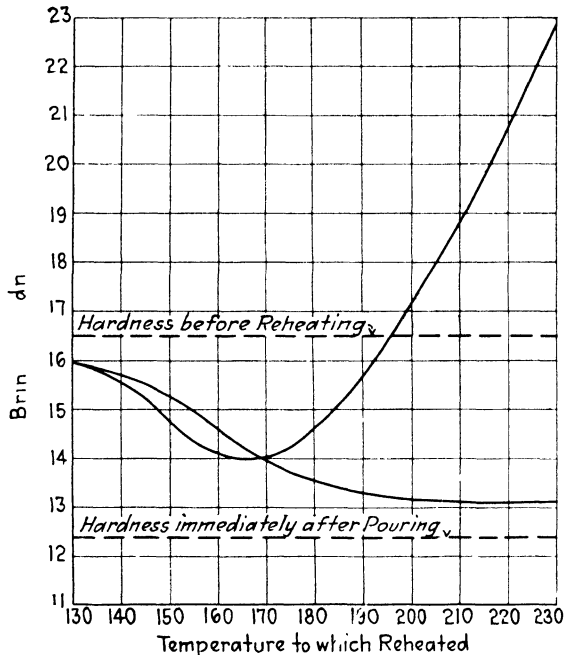


FIG. 35.—EFFECT OF REHEATING ON HARDNESS. CURVE 1 INDICATES HARDNESS IMMEDIATELY AFTER REHEATING. CURVE 2, HARDNESS 6 DAYS AFTER REHEATING.

5. Metal annealed above 216° C., reaged after 4 days to a greater hardness than the original cast sample.

F. R. PYNE, Perth Amboy, N. J.—In chemical work and electrolytic work it has always been customary to use a 6 to 10 per cent. antimony and lead alloy for tank linings, the idea being that it was tougher and stronger than most of the others. Judging from these curves here, particularly the one designated Fig. 25, the hardness is much lower than the 3, while it is higher than the 4, and in Fig. 4 the tensile strength of the 10 per cent. alloy is much less than it is from 2 to 4.

R. S. DEAN.—There is no question but that if you properly heat treat a 2 or 3 per cent. alloy you will have a higher tensile strength and hardness. There are some purposes for which a considerable amount of antimony is necessary.

R. S. ARCHER, Cleveland, O.—Several years ago we did some work on magnesium-rich alloys containing aluminum, and we also found that they showed this heat-treating and age-hardening effect. It is interesting to note that we found a rate of aging effect similar to that pointed out by Mr. Dean for the lead-antimony alloys; that is, we found that the age-hardening depended to quite an extent on the rate of cooling from the higher temperature or solution heat treatment. We did not find, however, that the extent of hardening differed as much as in the lead-antimony alloys. We found that the hardness attained was not greatly different but that the rate of attaining it was quite different.

We have always felt that there was some question about the use of the electrical conductivity method for investigating solubility. In the aluminum alloys the effects are not nearly as simple as in the lead-antimony alloys. The first age-hardening is accompanied very often by an increase in resistance, whereas precipitation would theoretically be accompanied by a decrease in resistance. The complete age-hardening at higher temperatures is nearly always accompanied by a decrease in resistance. We do not know why that is, but I might venture the suggestion that the arrangement of the precipitate is rather vital and that perhaps in the first stages of precipitation there is a more or less complete envelope precipitated around the grains which has a low specific conductivity, and that in the later stages that envelope breaks up and spheroidizes, allowing a decrease in electrical resistance to be manifested.

G. O. HIERS, New York, N. Y.—I would like to ask if the amount of the metal has a great effect upon the hardening?

R. S. DEAN.—Yes, it does have; if the metal is worked after the quenching, but before the hardening, it increases the speed of hardening and at the same time decreases the amount of hardening; that is, it acts in the same general way as an increase in temperature would do. It causes the particles of separated material to coalesce more rapidly and to a greater extent than would otherwise be the case.

G. O. HIERS.—How about the effect of the grain size before the heat treatment?

R. S. DEAN.—The old grains still remain, and we like to keep them as small as possible because the large grains are considerably more brittle.

J. S. McCLENAHAN, New York, N. Y.—How, with a $2\frac{1}{2}$ mixture, having a very good hardness feature, does the curve of expansion and

contraction work out with regard to the percentage of antimony and lead mentioned? Is the tendency to buckle greater or less?

R. S. DEAN.—We have not determined the coefficient of expansion. There is a small volume change which goes on with the hardening process; that is, as the alloy hardens, it increases in volume, but we have not determined the coefficient of expansion in either the hard or the soft state.

E. H. DARBY, Rome, N. Y.—Mr. Dean, have you carried your investigation along the line of the lead-tin-antimony alloy any further?

R. S. DEAN.—We have.

E. H. DARBY.—Do you find the same properties are present there?

R. S. DEAN.—The lead-tin alloy shows an age-hardening. We are making, and have made, investigations with antimony and tin alloys on which we hope to report later. At this time there is not a great deal to be said except that the lead-antimony-tin alloys do age-harden.

A Preliminary Study of Magnesium-base Alloys

By BRADLEY STOUGHTON* AND M. MIYAKE,† BETHLEHEM, PA.

(New York Meeting, February, 1926)

THE importance of magnesium alloys as engineering materials has increased rapidly in the past few years. The most important properties of magnesium alloys are their lightness and strength, which result in their extensive use in aircraft and automobile construction. Recent progress in the metallurgy of magnesium seems to offer hope of the production of the pure metal at a reasonable cost. The use of magnesium would doubtless increase greatly if it could be produced at a cost comparable with that of aluminum.

A preliminary survey of the magnesium-base alloys shows that the most promising from a practical standpoint are magnesium-aluminum and magnesium-zinc as binary alloys, and magnesium-zinc-aluminum as ternary alloys. The research reported in this paper is a preliminary study of binary magnesium-aluminum and magnesium-zinc alloys, as an introduction to a series of further investigations.

MAGNESIUM-ALUMINUM SYSTEM

The magnesium-aluminum system was first studied by Boudouard,¹ who merely determined the liquidus. An accepted constitutional diagram was given by Grube,² who found a compound Al_3Mg_4 (melting point = 462.7°C.) and two eutectics at 35 per cent. magnesium (451.6°C.) and at 68 per cent. magnesium (440°C.). Between the first eutectic and the compound a solid solution exists. This diagram was checked or supplemented by Pécheux,³ Broniewski,⁴ Eger,⁵ Schirmeister,⁶ Vogel⁷

* Professor of Metallurgy, Lehigh University.

† Graduate Student, Department of Metallurgy, Lehigh University.

¹ O. Boudouard: Sur les alliages d'aluminium et de magnésium. *Comp. Rend.* (1901) **132**, 1325; **133**, 1003; *Bull. Soc. Chim.* (1902) **27**, 5, 45.

² G. Grube: Über Magnesium-Aluminiumlegierungen. *Zeit. anorg. Chem.* (1905) **45**, 225.

³ H. Pécheux: Contribution à l'étude des alliages de l'aluminium. *Rev. Gén. Sci.* (1907) **18**, 109.

⁴ W. Broniewski: Sur les propriétés électriques des alliages aluminium-magnésium. *Comp. Rend.* (1911) **152**, 85.

⁵ G. Eger: Studie über die Konstitution der ternären Magnesium-Aluminium-Zink Legierungen. *Int. Zeit. Metallog.* (1913) **4**, 42.

⁶ H. Schirmeister: Ergänzung des Aluminium-Magnesium-Zustandsdiagrammes. *Metall u. Erz.* (1914) **11**, 522.

⁷ R. Vogel: Über ternäre Legierungen des Aluminiums mit Magnesium and Kupfer. *Zeit. anorg. Chem.* (1919) **107**, 265.

and Merica, Waltenberg, and Freeman.⁸

Recently this system was thoroughly studied and an excellent constitutional diagram was given by Hanson and Gayler.⁹ The diagram,

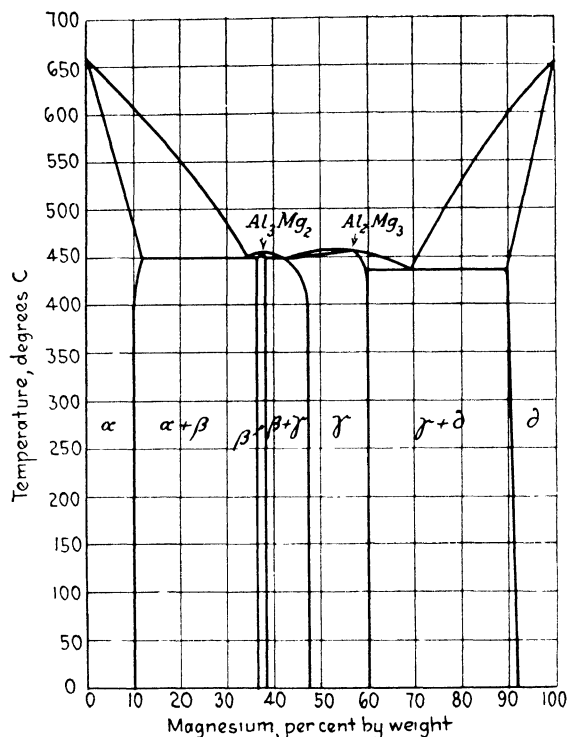


FIG. 1.—EQUILIBRIUM DIAGRAM OF HANSON AND GAYLER.⁹

modified considerably from those of earlier investigators, is shown in Fig. 1. There occur two compounds, Al_3Mg_2 and Al_2Mg_3 , and three eutectics. Both the pure metals and the compounds form solid solutions. The solid solubility of magnesium in aluminum is indicated as approximately 12 per cent. at 448° C. and 10 per cent. at room temperature. According to Merica and his associates,⁸ aluminum dissolves about 12.5

⁸ P. D. Merica, R. G. Waltenberg, and J. R. Freeman, Jr.: Constitution and Metallography of Aluminum and Its Light Alloys with Copper and with Magnesium. *Sci. Papers*, B. S. (1919) 337; *Trans. A. I. M. E.* (1920) **65**, 3.

⁹ D. Hanson and M. L. V. Gayler: Constitution of the Alloys of Aluminium and Magnesium. *Jnl. Inst. Metals* (1920) **24**, 201; *Engineering* (1920) **110**, 788, 819.

per cent. of magnesium as Mg_4Al_3 (really Al_3Mg_2) at 450°C . and the solubility of the compound decreases with decreasing temperature. At 300°C . the solubility is about 5.9 per cent. The later investigation of Ohtani¹⁰ shows the solid solubility is approximately 9.7 per cent. at 400°C . and 7.3 per cent. at 320°C . Mehl¹¹ studied electrically the beta + gamma field, and set the limit of the gamma field at 49.8 per cent. magnesium. According to Hanson and Gayler's diagram, the solid solubility of aluminum in magnesium is about 10 per cent. at 435°C ., decreasing somewhat as the temperature falls. The experiments by the Aluminum Co. of America,¹² however, show that the solubility at 435°C . is somewhat greater than 10 per cent., and that it decreases more rapidly with falling temperature. The diagram of Hanson and Gayler shows no indications of transformations below the temperature of the solidus.

MECHANICAL PROPERTIES OF MAGNESIUM-ALUMINUM ALLOYS

Aluminum seems to be the most favorable alloying metal for magnesium, because it not only has a low density, but is near to magnesium in the electrochemical series. The mechanical properties of the magnesium-aluminum alloys were fully investigated by the Dow Chemical Co., and jointly by the Aluminum Co. of America and the American Magnesium Corp. Dowmetal,^{13 to 18} sold by the Dow Chemical Co., is basically a series of alloys of magnesium and aluminum. The American Magnesium Corpn. sells various magnesium-aluminum alloys under the trade name of Greyhound brand.¹⁹

The more important mechanical properties of magnesium-aluminum alloys, as reported by Gann¹⁷ of the Dow Chemical Co., are shown in

¹⁰ B. Ohtani: Alloys of Aluminium-Magnesium. *Jnl. Chem. Ind.* [Japan] (1922) **25**, 36.

¹¹ R. F. Mehl: Preparation of Pure Alloys. *Trans. Am. Electrochem. Soc.* (1924) **46**, 149.

¹² "Magnesium." A Handbook by the American Magnesium Corpn., Niagara Falls, N. Y., 1923.

¹³ Anon: New Light Piston Alloy. *Automot. Ind.* (1919) **41**, 161.

¹⁴ E. J. Jenkins: The New Alloy of Magnesium. *Iron Age* (1920) **106**, 193.

¹⁵ G. Gaulois: A New Magnesium Alloy for Motor Pistons. *Sci. Am.* (1920) **123**, 519.

¹⁶ Anon: New Light Piston Alloy, Dowmetal. *Automot. Ind.* (1920) **42**, 967.

¹⁷ J. A. Gann: Dowmetal and Its Applications. *Trans. Am. Soc. Steel Treat.* (1922) **2**, 607.

¹⁸ J. A. Gann: Recent Progress in Magnesium Alloys. *Jnl. Ind. & Eng. Chem.* (1922) **14**, 864, *Raw Material* (1922) **5**, 394.

¹⁹ S. K. Colby: Marketing Magnesium. *Eng. & Min. Jnl.-Pr.* (1924) **118**, 51.

Fig. 2. The curves *A* refer to cast metal and *B* to metal heat treated for two hours at 800° F. (427° C.). The curves showing per cent. elongation and per cent. reduction in area have been omitted. They both begin at about 5 per cent. for pure magnesium, rise rapidly to 8 to 10 per cent. at an aluminum content of 4 per cent., and gradually decrease to 1 per cent. at 12 per cent. aluminum. The Brinell hardness is roughly proportional to the aluminum content, varying from 35 to 40 for pure magnesium up to 140 to 150 for a 30 per cent. aluminum alloy.

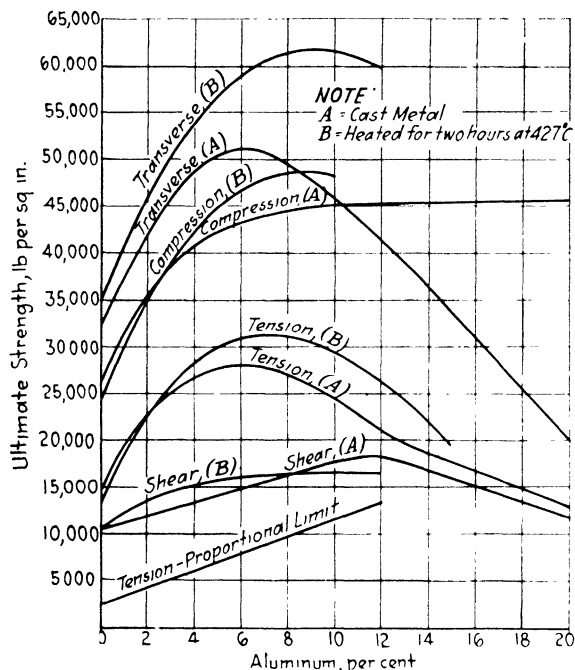


FIG. 2.—STRENGTH OF SOME ALLOYS OF MAGNESIUM WITH ALUMINUM, GANN.⁷ (A) CAST METAL, (B) HEATED FOR 2 HR. AT 427° C.

In Fig. 3, the data given by the joint research of the Aluminum Co. of America and the American Magnesium Corpn.^{12,20} are shown. The curves *A* refer to sand-cast metal and *B* to extruded metal. The results are approximately in agreement with those of Gann, and show the superiority of the 4 per cent. to 12 per cent. aluminum alloys. The alloys can be materially improved in mechanical properties by mechanical working. Almost the same figures are obtained by rolling as by extrusion. Aitchison²¹ gave the figures of Table 1 for the 6 per cent. aluminum alloy.

²⁰ Anon: Magnesium. *Chem. & Met. Eng.* (1924) **31**, 383.

²¹ L. Aitchison: Mechanical Properties of Magnesium Alloys. *Jnl. Inst. Metals* (1923) **29**, 17; *Engineering* (1923) **115**, 312; *Metal Ind.* (N. Y.) (1923) **21**, 279; *Metal Ind.* (Lond.) (1923) **22**, 222; *Min & Met.* (1923) **4**, 288.

TABLE 1.—*Alloy of Magnesium with 6 Per Cent. Aluminum*

	ELASTIC LIMIT, LB. PER SQ. IN.	YIELD POINT, LB. PER SQ. IN.	ULTIMATE STR., LB. PER SQ. IN.	ELONGATION, PER CENT.
Cast bar. . . .	4,000	12,200	24,000	5.0
Rolled strip. .	12,500	37,200	41,500	7.5
Extruded rod.			42,000	

The strength of these alloys can be further increased by chill-casting. Maybrey²² gave the results shown in Table 2.

TABLE 2

	PURE MAGNESIUM ULTIMATE STR., LB. PER SQ. IN.	ELONGATION, PER CENT.	6 PER CENT ALUMINUM ULTIMATE STR., LB. PER SQ. IN.	ELONGATION, PER CENT.
Chill-cast.	17,700	4	25,800	5
Sand-cast.	15,200	5	20,000	7

The magnesium-aluminum alloys not only possess excellent mechanical properties, but have a remarkably low density even in the 12 per cent. aluminum alloy. The density of the alloys is given in Table 3.^{12,20,23}

TABLE 3.—*Density of Magnesium-aluminum Alloys*

Aluminum, per cent	0	2	4	6	8	10	12
Density.	1.74	1.75	1.77	1.78	1.79	1.81	1.82

The Dow Chemical Co. recommends the 8 per cent. aluminum alloy for casting purpose, and calls it Dowmetal "A." The physical and mechanical properties of Dowmetal "A" are given in Table 4.

TABLE 4.—*Dowmetal "A"*

Tensile strength	25,000 lb. per sq. in.
Elongation.	4 per cent.
Specific tenacity.	14,000 lb. per sq. in.
Compressive strength.	44,000 lb. per sq. in.
Brinell hardness.	55
Thermal conductivity (20°–350° C.)	0.200
Thermal expansion (20°–400° C.)	0.29×10^{-4}
Melting point.	615° C.
Specific gravity.	1.8

HEAT TREATMENT OF MAGNESIUM-ALUMINUM ALLOYS

The magnesium alloys containing 4 per cent. or more aluminum can be improved in mechanical properties by a suitable heat treatment.

²² H. J. Maybrey: Magnesium in the Foundry. *Foundry Trade Jnl.* (1923) **28**, 227; *Metal Ind.* (N. Y.) (1923) **21**, 398; *Metal Ind.* (Lond.) (1923) **23**, 315; *Foundry* (1924) **52**, 96; *Mech. World* (1924) **75**, 12.

²³ L. Aitchison: Materials in Aircraft Construction. *Jnl. Royal Aeronaut. Soc.* (1924) **28**, 238; *Proc. Inst. of Auto. Eng.* (1924) **18**, 557; *Automotive Ind.* (1924) **50**, 924, 970.

It is reported by Gann,¹⁷ and by the Aluminum Co. of America and American Magnesium Corp'n.¹² that the strength and elongation of cast alloys are improved by heating the alloys for some hours at a temperature in the vicinity of 425° C. According to Gann, complete solid solution is produced in the 8 per cent. aluminum alloy in 4 hr. at 820° F. (438° C.) while 24 hr. are required at 750° F. (400° C.). However, the maximum increase in strength occurs long before complete solid solution is

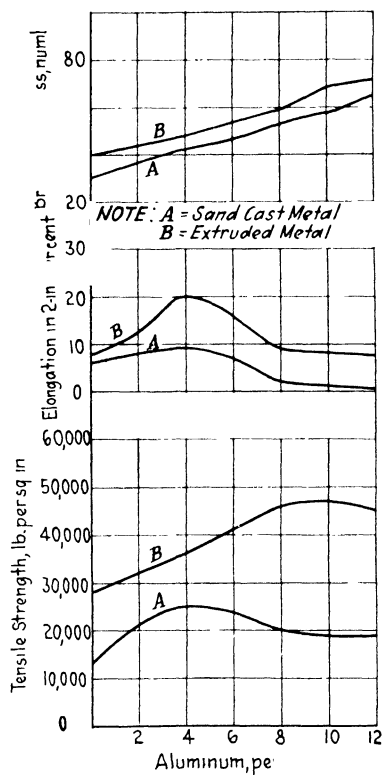


FIG. 3.—SOME MECHANICAL PROPERTIES OF SOME ALLOYS OF MAGNESIUM WITH ALUMINUM.^{12, 20} (A) SAND-CAST METAL; (B) EXTRUDED METAL.

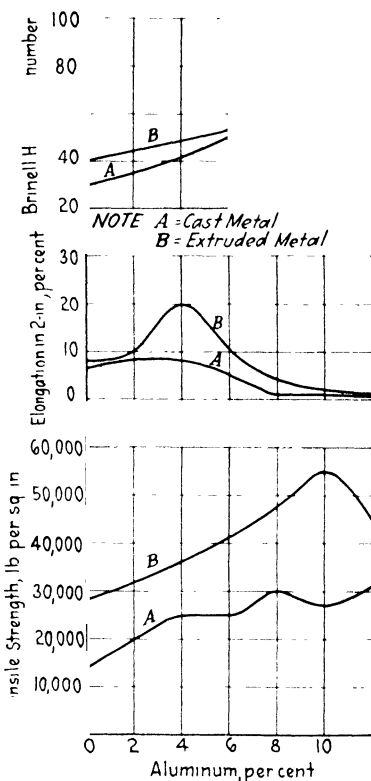


FIG. 4.—SOME MECHANICAL PROPERTIES OF MAGNESIUM-ALUMINUM ALLOYS AFTER ARTIFICIAL AGING.^{12, 20} (A) CAST METAL; (B) EXTRUDED METAL.

reached, although some eutectic is left undissolved. As shown in Figs. 2, 3, and 4, not only do heat treatment and mechanical treatment increase the strength of the alloy; they shift the position of the maximum tensile strength towards higher aluminum alloys. The per cent. elongation curve is the same as for the original castings up to 2 per cent. aluminum, and then follows the same tendency to shift the maximum as the other heat-treated curves, while the Brinell hardness is slightly lowered by the

heat treatment. The Aluminum Co. of America and American Magnesium Corp'n. explain that the improvement in strength and elongation by this heat treatment is due to the solution of free magnesium-aluminum compound.

According to the Aluminum Co. of America and American Magnesium Corp'n., if the alloy, either cast or worked, is cooled rapidly after this heat treatment and is reheated to a temperature of from 150° to 250° C. for a number of hours, the magnesium-aluminum compound precipitates out of solid solution in very small particles and causes hardening. This fact is quite analogous to the hardening and increasing in strength of aluminum-copper alloys by the quenching followed by



FIG. 5.—AL 4 PER CENT., SAND-CAST. $\times 100$. ETCHED WITH 2 PER CENT. HNO_3 .



FIG. 6.—AL 4 PER CENT., CHILL-CAST. $\times 100$. ETCHED WITH 2 PER CENT. HNO_3 .

so-called "artificial aging," advanced by Archer and Jeffries.²⁴ An example of the mechanical properties of magnesium-aluminum alloys subjected to this artificial-aging treatment after quenching is shown in Fig. 4.^{12,20} In those curves, *A* refers to cast alloys and *B* to extruded alloys. It will be noted that the maximum strength in these alloys is 55,000 lb. per sq. in. obtained from 10 per cent. aluminum alloy extruded, quenched, and artificially aged. The corresponding elongation is only 2 per cent. The highest value for elongation is 20 per cent. with 4 per cent. aluminum alloy as extruded, or extruded, quenched, and artificially aged, and the corresponding strength is 36,000 lb. per sq. in.

MICROSTRUCTURES OF MAGNESIUM-ALUMINUM ALLOYS

The microstructures of sand-cast and chill-cast alloys are shown in Figs. 5 to 10. The grains of delta solid solution are partly or entirely

²⁴ R. S. Archer and Z. Jeffries: New Developments in High-strength Aluminum Alloys. *Trans. A. I. M. E.* (1925) 71, 828.

surrounded by the eutectic. The size of grain and the amount of eutectic depend on the content of aluminum and the rate of cooling. In



FIG. 7.—AL 8 PER CENT., SAND-CAST. $\times 100$. ETCHED WITH 2 PER CENT. HNO_3 .

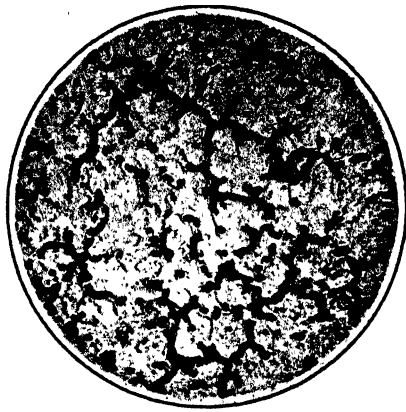


FIG. 8.—AL 8 PER CENT. CHILL-CAST. $\times 100$. ETCHED WITH 2 PER CENT. HNO_3 .

the alloys having higher content of aluminum and more rapidly cooled, the amount of eutectic is greater and the size of grain is smaller. It will be seen in Fig. 1 that magnesium can hold nearly 10 per cent. aluminum

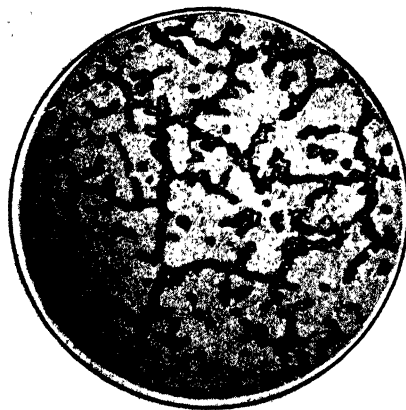


FIG. 9.—AL 12 PER CENT., SAND-CAST. $\times 100$. ETCHED WITH 2 PER CENT. HNO_3 .

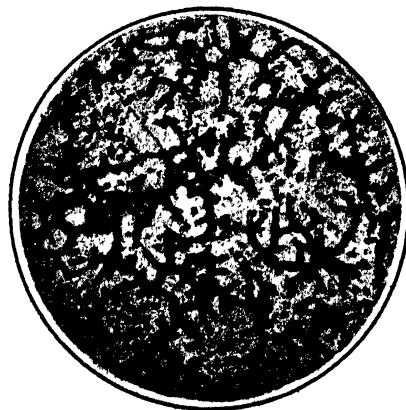


FIG. 10.—AL 12 PER CENT., CHILL-CAST. $\times 100$. ETCHED WITH 2 PER CENT. HNO_3 .

in solid solution. The castings have cooled so rapidly, however, that there was not sufficient time for complete equilibrium to be established, and even the lower per cent. aluminum alloys retain some eutectic.

A hardness test (Brinell, 500 kg., 10 mm., 30 sec.) shows that the hardness of the alloys is directly proportional to the amount of eutectic and inversely proportional to the size of grain. The Brinell hardness of the cast alloys is shown in Table 5.

TABLE 5.—*Brinell Hardness of Magnesium-aluminum Alloys*

ALUMINUM, PER CENT.	SAND-CAST	CHILL-CAST
4	44	49
6	49	57
8	55	65
10	59	74
12	65	80

FIG. 11.

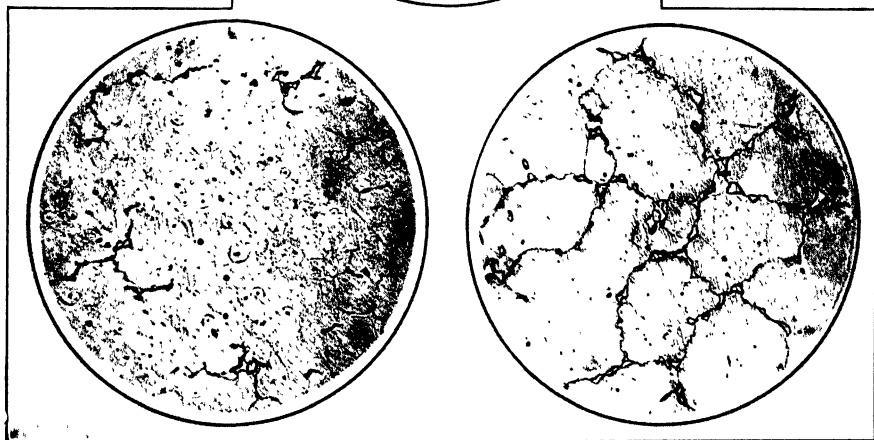
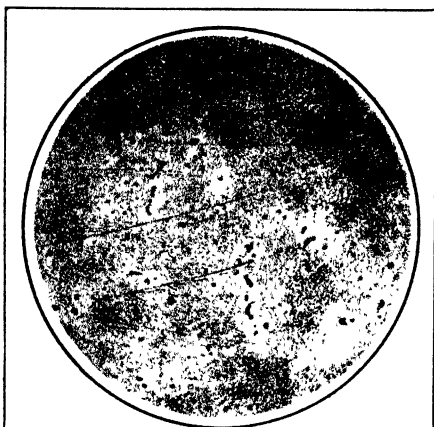


FIG. 12.

FIG. 13.

FIG. 11.—AL 4 PER CENT., SAND-CAST, HEAT-TREATED. $\times 100$. ETCHED WITH 2 PER CENT. HNO_3 .

FIG. 12.—AL 8 PER CENT., SAND-CAST, HEAT-TREATED. $\times 100$. ETCHED WITH 2 PER CENT. HNO_3 .

FIG. 13.—AL 12 PER CENT., SAND-CAST, HEAT-TREATED. $\times 100$. ETCHED WITH 2 PER CENT. HNO_3 .

As previously stated, the alloys can be improved in mechanical properties by simple heating at a temperature somewhat below the solidus. In Figs. 11 to 13, the microstructures of sand-cast alloys heat treated at 430° C. for 2 hr. are shown. It will be noted that the size of grain grows and the amount of eutectic decreases. As already stated, the higher aluminum alloys can be hardened by quenching from a temperature below the solidus followed by an artificial aging at a temperature between 150° and 250° C. In order to obtain the best mechanical properties an extended period of time of heating and reheating may be required, but it was not feasible to test this question during the present investigation. Results were obtained of the change of hardness of the alloys due to heating for 2 hr. at 430° C., quenching in water, and reheating for 4 hr. at 170° C. The results of Brinell hardness test, as shown in Table 6, exhibit a material increase of hardness in the 12 per cent. aluminum alloy, especially in the chill-cast alloy.

TABLE 6.—*Brinell Hardness of Some Magnesium-aluminum Alloys*

Aluminum, Per Cent.	Sand-cast		Chill-cast	
	Original Castings	Quenched and Reheated	Original Castings	Quenched and Reheated
4	44	45	49	48
6	49	49	57	55
8	55	57	65	62
10	59	70	74	86
12	65	79	80	100

The alloys, when aged at the room temperature for seven days after quenching, did not show any change in hardness. The microstructures of the sand- and chill-cast alloys with 12 per cent. aluminum, before and after the artificial aging, are shown in Figs. 14 to 17.

Some difficulty was experienced at first in developing the structure of these alloys. The most satisfactory method seems to be to rub the polished surface of the specimens a few times with a swab of cotton wetted with a 2 per cent. alcoholic solution of nitric acid. All the photographs shown were etched by this method.

MAGNESIUM-ZINC SYSTEM

The magnesium-zinc system was first studied by Boudouard,²⁵ who merely determined the liquidus. An accepted constitutional diagram

²⁵ O. Boudouard: Les alliages de zinc et de magnésium. *Comp. Rend.* (1904) **139**, 424.

was given by Grube,²⁶ which was checked by Bruni, Sandonnini, and Quercigh,²⁷ Eger,²⁸ and Pierce.²⁹

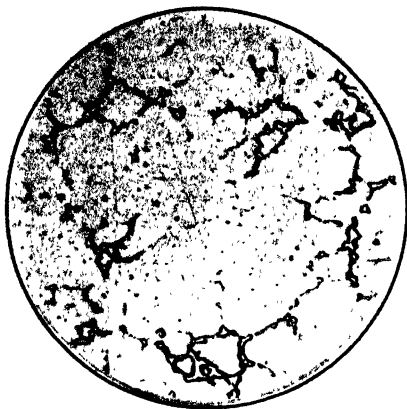


FIG. 14.—Al 12 PER CENT, SAND-CAST, QUENCHED. $\times 100$. ETCHED WITH 2 PER CENT. HNO_3 .

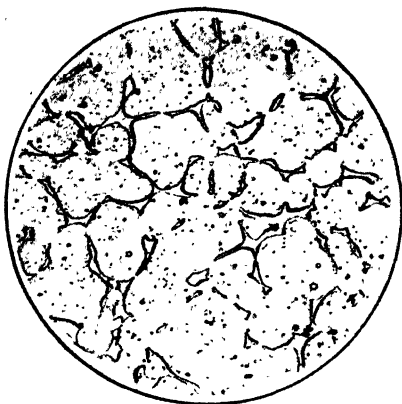


FIG. 15.—Al 12 PER CENT. CHILL-CAST, QUENCHED. $\times 100$. ETCHED WITH 2 PER CENT. HNO_3 .

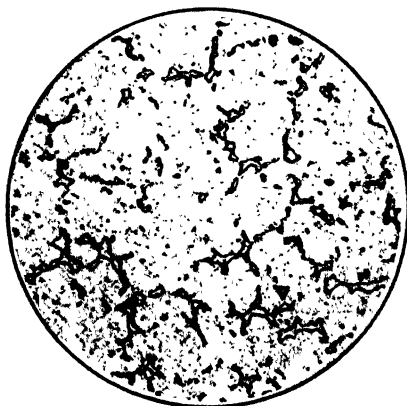


FIG. 16.—Al 12 PER CENT, SAND-CAST, REHEATED. $\times 100$. ETCHED WITH 2 PER CENT. HNO_3 .

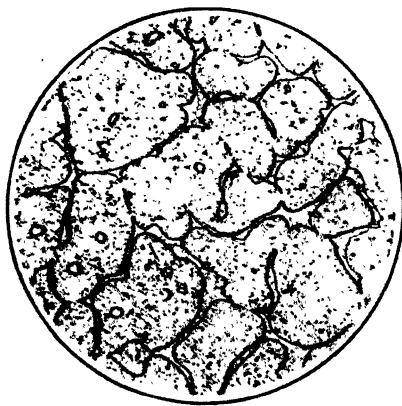


FIG. 17.—Al 12 PER CENT, CHILL-CAST, REHEATED. $\times 100$. ETCHED WITH 2 PER CENT. HNO_3 .

The Grube-Eger diagram is shown in Fig. 18. It shows a compound, MgZn_2 (590°C.) and two eutectics, one at 51.1 per cent. zinc (355°C.)

²⁶ G. Grube: Über die Legierungen des Magnesium mit Kadmium, Zink, Wismut und Antimon. *Zeit. anorg. Chem.* (1906) **49**, 77.

²⁷ G. Bruni, C. Sandonnini and E. Quercigh: Über die ternären Legierungen von Magnesium, Zink und Kadmium. *Zeit. anorg. Chem.* (1910) **68**, 78.

²⁸ G. Eger: Studie über die Konstitution der ternären Magnesium-Aluminium-Zink Legierungen. *Int. Zeit. Metall.* (1913) **4**, 46.

²⁹ W. M. Peirce: Studies on the Constitution of Binary Zinc-base Alloys. *Trans. A. I. M. E.* (1923) **68**, 781.

and the other at 96 per cent. zinc ($369^{\circ}\text{C}.$). This diagram has been confirmed by Pierce; namely, that there is no solubility on the zinc side, but it misses a solid solution on the magnesium side, which one of us has noted, as follows: At the eutectic temperature, magnesium holds more than 10 per cent. of zinc in solid solution. This solubility decreases as

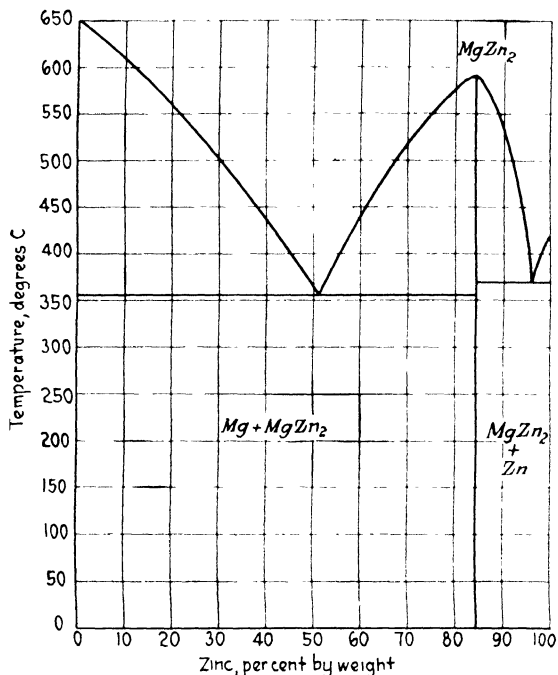


FIG. 18.—GRUBE-EGER EQUILIBRIUM DIAGRAM OF MAGNESIUM-ZINC ALLOYS.

the temperature drops. This observation is important in connection with the heat treatment of the magnesium-zinc alloys.

MECHANICAL PROPERTIES OF MAGNESIUM-ZINC ALLOYS

The mechanical properties of magnesium-zinc alloys seem to resemble those of the magnesium-aluminum alloys. The tensile strength and specific gravity, as given by Aitchison,²³ are shown in Table 7.

TABLE 7.—*Tensile Strength and Specific Gravity of Magnesium-zinc Alloys*

ZINC, PER CENT.	MAX. STRENGTH, LB. PER SQ. IN.	SP. GR.
4	12,300	1.78
5	13,500	1.79
6	17,200	1.81
7	21,000	1.82
8	25,000	1.84
9	21,300	1.85
10	18,000	1.87
11	17,200	1.89
12	16,600	1.91

According to the Dow Chemical Co.,³⁰ the 5 per cent. zinc sand-cast alloy has the following mechanical properties:

Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent.	Brinell Hardness
25,600	7.4	41

Maybrey²² reports that the 8 per cent. zinc alloy has the mechanical properties shown in Table 8.

TABLE 8

	TENSILE STRENGTH, LB PER SQ. IN.	ELONGATION PER CENT.
Chill-cast	24,200	3
Sand-cast	20,400	4

"Elektron,"^{18,21,31 to 46} made by the Chemische Fabrik Griesheim-Elektron, Frankfurt a. M., Germany, is practically a series of magnesium-zinc alloys. Their analyses are summarized as follows:

³⁰ Physical Properties of Materials. *Circ.* 101, Bur. of Stds. (1924) 124.

³¹ F. Thomas: Über das Vergiessen von Elektronmetall. *Stahl u. Eisen* (1920) **40**, 290; *Elekt. u. Masch.* (1920) **38**, 306; *Brass Wld.* (1920) **16**, 342; *Metal Ind.* [Lond.] (1920) **17**, 107.

³² Anon.: New High Magnesium Alloys. *Automotive Ind.* (1920) **42**, 1343.

³³ Anon.: Electron. *Tech. Rev.* (1921) **8**, 162.

³⁴ S. Beckinsale: The Magnesium Alloy: Electron. *Jnl. Inst. Metals* (1921) **26**, 375; *Metal Ind.* [N. Y.] (1921) **19**, 433; *Metal Ind.* [Lond.] (1921) **19**, 305; *Engineering* (1921) **112**, 641; *Foundry* (1921) **49**, 821; *L'Electrician* (1922) **53**, 297.

³⁵ E. Weinwurm: Das Elektronmetall. *Chem. Zeit.* (1921) **45**, 579; *Elekt. u. Masch.* (1921) **39**, 516; *Génie Civil* (1921) **79**, 593.

³⁶ C. Girard: Les alliages légers et leur emploi en aéronautique. *Bull. Soc. d'Enc.* (1921) **133**, 863; *Rev. Mét.* (1921) **18**, 567; *Rev. Gén. Elec.* (1921) **10**, 27; *Chem. & Met. Eng.* (1922) **26**, 798.

³⁷ A. Bregman: Electron Metal. *Met. Ind.* [N. Y.] (1922) **20**, 1.

³⁸ Anon.: Magnesium Alloys in Engineering. *Prac. Eng.* (1922) **65**, 404.

³⁹ L. Guillet: Les alliages légers: Leurs récents progrès. *Rev. Mét.* (1922) **19**, 688.

⁴⁰ C. Irresberger: Magnesiumguss. *Giesserei Zeit.* (1922) **19**, 599; *Mech. Eng.* (1923) **45**, 48.

⁴¹ A. Porterin: Le magnésium et les alliages ultra-légers. *Bull. Soc. Ing. Civils* (1923) **76**, 486; *Rev. Mét.* (1923) **20**, 428; *Génie Civil* (1923) **82**, 452.

⁴² H. Kalpers: Le métal électron. *Fond. Mod.* (1923) **17**, 74.

⁴³ F. Thomas: Fortschritte und Aussichten in der Verwendung der Lichtmetalle *Maschinenbau* (1923) **2**, G 85.

⁴⁴ R. R. Moore: Resistance of Manganese Bronze, Duralumin, and Elektron Metal to Alternating Stresses. *Proc. Am. Soc. Test Mat.* (1923) **23**, 106; *Metal Ind.* [Lond.] (1923) **23**, 50.

⁴⁵ F. H. Schulz: Die Nichteisenmetalle unter besonderer Berücksichtigung der Luftfahrzeuge. *Zeit. Ver. deut. Ing.* (1924) **68**, 545.

⁴⁶ G. Schreiber and R. Neuwahl: Elektronmetall. *Maschinenbau* (1925) **4**, 7.

Mg.	91.59-95.34	Cu.....	0-0.74
Zn..	4.24- 7.64	Sn.....	0-0.35
Al..	0- 1.60	Mn.....	0-0.08

The more important physical and mechanical properties of a few kinds of "Elektron" are given in Table 9.

TABLE 9.—*Physical and Mechanical Properties of Elektron*

	ZI Wrought Alloy		VI Specially Hard, Strong Alloy		
	AZ Cast Alloy	Extruded	Hard-rolled	Extruded	Extruded and Hammered
Elastic limit, lb. per sq in.....	4,300- 7,000	8,500-10,000		31,000	38,000
Proportional limit, lb. per sq. in.....	8,500-13,000	21,000-26,000		40,000-43,000	45,500 48,000
Tensile strength, lb per sq. in.	17,000-21,000	37,000-40,000	41,000-45,500	48,000-51,000	60,000 63,000
Elongation, per cent....	2- 4	18-22	2- 3	10-12	3-5
Compressive strength, lb. per sq in.	38,000-40,000	50,000		58,000	77,000
Brinell hardness	44-46	46-50	56-65	75	90
Electric conductivity .	15-16	16-18			
Thermal conductivity.	0 32	0 32			
Specific heat	0 24	0 24			
Thermal expansion		0 000026			
M. P., degrees Centi- grade	630	635			
Specific gravity	1.80	1 81		1.83	

"Elektron" can be extruded, rolled or drawn at 400° C., and forged at 220° to 250° C. Cold working causes brittleness, but the ductility is recovered on annealing.

HEAT TREATMENT OF MAGNESIUM-ZINC ALLOYS

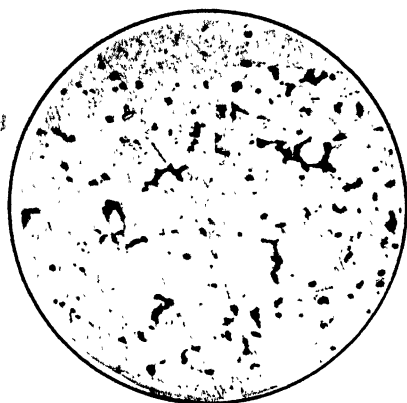
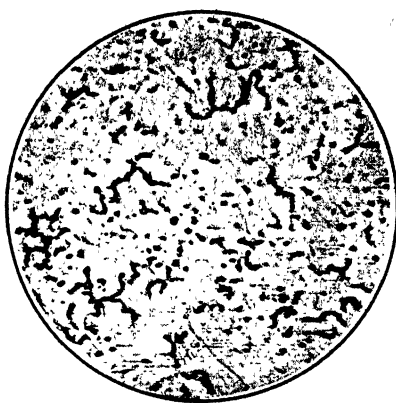
The mechanical properties of magnesium-zinc alloys may be improved by a suitable heat treatment just as in the magnesium-aluminum alloys. The most important fact discovered by one of the authors is that the magnesium-zinc alloys can be hardened materially by quenching from a temperature somewhat below the solidus, followed by reheating to a temperature higher than room temperatures (so-called artificial aging). No hardening effect occurs when the alloys are aged at room temperatures for several days after quenching. An enormous increase in hardness is obtained by heating some of the magnesium-zinc alloys for 2 hr. at 340° C., quenching in water, and then reheating for 4 hr. at 150° C. This is shown in Table 10.

It will be seen that the effect is especially great in high-zinc and chill-cast alloys. By the proper selection of temperature and time, excellent results may be expected. The effect of quenching and reheating the magnesium-zinc alloys, together with the solubility of $MgZn_2$ in magne-

TABLE 10.—*Brinell Hardness of Quenched and Artificially Aged Alloys of Magnesium and Zinc*

Zinc, Per Cent.	Sand-cast		Chill-cast	
	Original Castings	Quenched and Reheated	Original Castings	Quenched and Reheated
5	43	47	48	57
8	50	58	57	70
10	54	67	63	85
12	57	76	69	93

sium, offers an important subject for research, which we hope to be able to prosecute at some future time.

FIG. 19.—Zn 8 PER CENT., SAND-CAST. $\times 100$. ETCHED WITH 2 PER CENT. HNO_3 .FIG. 20.—Zn 8 PER CENT., CHILL-CAST. $\times 100$. ETCHED WITH 2 PER CENT. HNO_3 .FIG. 21.—Zn 12 PER CENT., SAND-CAST. $\times 100$. ETCHED WITH 2 PER CENT. HNO_3 .FIG. 22.—Zn 12 PER CENT., $\times 100$. ETCHED WITH 2 PER CENT. HNO_3 .

MICROSTRUCTURES OF MAGNESIUM-ZINC ALLOYS

The microstructure of sand- and chill-cast alloys containing 8 and 12 per cent. zinc are shown in Figs. 19 to 22. The structures resemble those of magnesium-aluminum alloys, the grains of magnesium-rich solid solution being partly or entirely surrounded by the eutectic.



FIG. 23.—Zn 12 PER CENT., SAND-CAST, QUENCHED. $\times 100$. ETCHED WITH 2 PER CENT. HNO_3 .

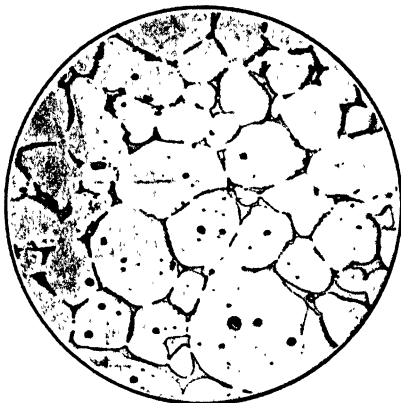


FIG. 24.—Zn 12 PER CENT., CHILL-CAST, REHEATED. $\times 100$. ETCHED WITH 2 PER CENT. HNO_3 .

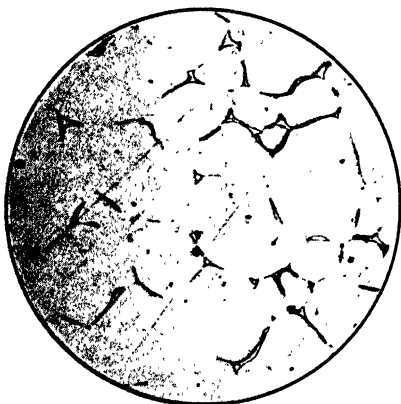


FIG. 25.—Zn 12 PER CENT., SAND-CAST, REHEATED. $\times 100$. ETCHED WITH 2 PER CENT. HNO_3 .

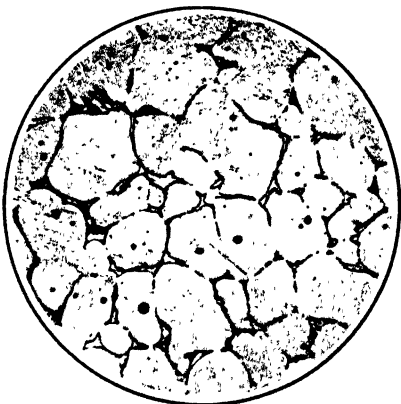


FIG. 26.—Zn 12 PER CENT., CHILL-CAST, QUENCHED. $\times 100$. ETCHED WITH 2 PER CENT. HNO_3 .

As previously stated, the magnesium-zinc alloys can be hardened by quenching followed by reheating. The microstructures of 12 per cent. zinc alloys, heated at 340°C . for 2 hr. and quenched in water, are shown in Figs. 23 and 26; and reheated to 150°C . for 4 hr. in Figs. 24 and 25.

That there exists a solid solution on the magnesium side is mentioned previously. The structures of 8 per cent. zinc sand-cast alloys, heated for seven hours at 340° C., and cooled in the air, and of 12 per cent. zinc sand-cast alloy, heated for 50 hr. at 340° C. and quenched in water, are shown in Figs. 27 and 28. In the alloys containing less than 10 per cent. zinc, heated for 50 hr. at 340° C., the eutectic can no longer be found.

The alloys were etched with 2 per cent. alcoholic solution of nitric acid in the same manner as the magnesium-aluminum alloys.

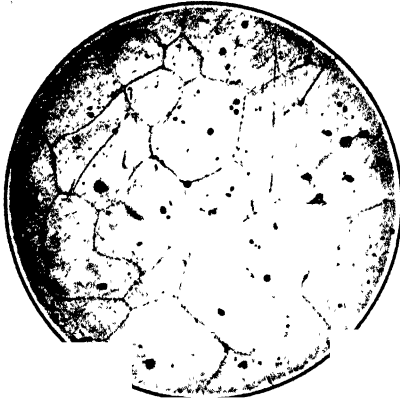


FIG. 27.—Zn 8 PER CENT. SAND, HEATED FOR 7 HR. $\times 100$. ETCHED WITH 2 PER CENT. HNO_3 .



FIG. 28.—Zn 12 PER CENT., SAND, HEATED FOR 50 HR. $\times 100$. ETCHED WITH 2 PER CENT. HNO_3 .

SUMMARY

The constitutional diagram and mechanical properties of magnesium-aluminum alloys are reviewed.

A metallographical study of magnesium-aluminum alloys is offered.

The constitutional diagram of magnesium-zinc alloys is reviewed, suggesting the existence of a solid solution on the magnesium side.

The mechanical properties of magnesium-zinc alloys, including "Elektron," are reviewed.

It was found that the magnesium-zinc alloys can be hardened by quenching in water from a temperature somewhat below the solidus, followed by reheating to a temperature higher than room temperature.

A metallographical study of magnesium-zinc alloys is offered.

DISCUSSION

S. DANIELS, Dayton, O. (written discussion).—I wish to call the attention of the authors to my publication on "Magnesium and Its Alloys" in the *Journal* of the American Society of Mechanical Engineers, Vol. 47, page 796, 1925.

The statement that the lightness and strength of magnesium alloys has led to their extensive use in aircraft and automobile construction is far too strong, at least insofar as it applies to aircraft work, for with these advantageous properties there are also the disadvantages to confront. In this last industry the use of magnesium-base alloy is still in the experimental stage, but the situation is promising enough to warrant the belief that some application will be found for cast materials and possibly for the wrought.

The analysis range of "Elektron" alloys given on page 554 is not in accord with the composition of the casting alloys which have been currently supplied by Germany. Three distinct classes of materials have been noted and the range of analysis covers a zinc content of from 1 to 6 per cent. and an aluminum content of from 2 to 6 per cent., with the ordinary impurities.

It is interesting to note that the magnesium-zinc alloys are susceptible to heat treatment. Perhaps this discovery can be beneficially applied to the magnesium-aluminum-zinc series.

Mention should be made of the 87 magnesium—13 copper alloy, which is a possible material for parts operating at elevated temperatures and for certain bearings.

B. STOUGHTON.—There is an interesting feature which is not on this diagram, and that is that the magnesium will carry 10 per cent. of zinc in solid solution, at a temperature of a little over 350° C., and that percentage decreases with decreasing temperature.

The existence of a solid solution and the fact that it decreases with falling temperature, has made it possible to apply heat treatment to these alloys so as to strengthen them, and notably heat treatment followed by artificial aging, because in this case also the alloys appear to be so immobile at atmospheric temperature that there is no breaking up of solution by standing at the ordinary atmospheric temperatures; they have to be artificially aged a little bit.

A. E. WHITE, Ann Arbor, Mich.—A criticism made by automobile men with regard to the magnesium base alloys, aside from the question of price, is the fact that they are not assured, at the present time, that they would be able to get enough metal to take care of their needs. Of course, if there is a demand for this metal, there is no question whatsoever but what there will be increased production.

R. S. DEAN, Chicago, Ill.—I was interested in Prof. Stoughton's statement that the quenched or rapidly-cooled alloys apparently showed less solubility, as if there were apparently more separation of eutectic. How was that determined? Is not the explanation of that the same as we found in lead-antimony alloys, that the more rapidly you quenched them, the more rapidly the material broke down. In other words, I wonder if it

is not a matter of rate; not that there is an actual change in the solubility with rapid quenching, but that when you quench, the material comes out of solution much more rapidly, so that there is an apparent lowering of solubility.

B. STOUGHTON.—That was determined by means of the micrographs. A good many microsections were studied and some were photographed and are given in the paper. I confess that I was greatly puzzled by the question. It seems to me that perhaps you have the explanation; that is to say, that it is a case of rate of breaking up. Mr. Miyake says that equilibrium is not established.

C. R. HAYWARD, Cambridge, Mass.—You speak of annealing above 350° C. That obviously means that melting does not begin, as you would expect it would according to this diagram. (See Fig. 18.)

B. STOUGHTON.—No, but you can go above 350° without getting to the solidus.

H. H. RICHARDSON, New Kensington, Pa.—What physical tests were used in determining the age-hardening after the solution treatment of these alloys?

B. STOUGHTON.—The Brinell hardness only was used.

H. H. RICHARDSON.—I think any one who looks at the diagram of aluminum-magnesium equilibrium is struck by its symmetry. (Fig. 18.) We have done some work at the Aluminum Co. of America laboratories on the 10 per cent. magnesium alloy with aluminum base, and found that on quenching 10 per cent. magnesium alloys, we got a considerable increase in hardness over the chilled-cast condition. We also found it possible to artificially age that to a very marked extent. We raised the Brinell hardness from 74 to over 100, which is in the range of the treated duralumins. The strange part about it, however, was that although we could take a quenched 10 per cent. magnesium alloy having a tensile strength of 35,000 lb. and a Brinell hardness of 74 to 75, age that and raise its Brinell hardness to about 100, we could not increase its tensile strength at all, and I wondered if perhaps your age-hardness treatment was different from ours, also whether you confined your tests only to the Brinell reading.

We found that there was an increase in Brinell hardness which was commensurate with the amount precipitated out of solution. However, the alloy became so brittle that it was worthless from a factory standpoint. The precipitate was very marked and is easily seen at 500. However, it has a very different appearance from O.L. and aluminum 2. I wonder if that situation holds with the 10 per cent. aluminum alloy.

L. ZICKRICK, Chicago, Ill.—Were the corrosion properties of these alloys investigated; that is was any difference in corrosion observed before heat treatment?

B. STOUGHTON.—We made no corrosion test.

Equilibrium Relations in Aluminum-copper Alloys of High Purity

By E. H. DIX, JR.,* AND H. H. RICHARDSON,† NEW KENSINGTON, PA.

(New York Meeting, February, 1926)

OF all the alloying elements used in commercial aluminum alloys, copper stands out as by far the most important, and it is perhaps for this reason that the constitution of the aluminum-copper system has received the attention of a number of experimenters covering a period of approximately 20 years. It would be expected that during this time the equilibrium relations would have been thoroughly and exactly worked out. In a general way this is true, but there is a surprising lack of agreement in the details of the high aluminum end of the diagram, particularly in regard to the solid solubility of copper in aluminum, which has been given variously as 2 per cent. to 5 per cent. at the eutectic temperature. The importance of this is much greater than might at first appear to one unfamiliar with modern commercial aluminum alloys. This is true because, with one exception, the susceptibility of the strong alloys to heat treatment depends, in part at least, upon the solid solubility relations of copper in aluminum.

In 1919, Merica, Waltenberg, and Freeman¹ published the first detailed information on these solubility relations. They found that the solubility of copper decreases with falling temperature from about 4 per cent. at 525° C. to about 1 per cent. at 300° C. and is apparently still diminishing at lower temperatures.

In 1921 there was published a brief account of the results obtained in the National Physical Laboratory, Teddington, England.² This laboratory, however, reported that 5 per cent. of copper is soluble in aluminum at 540° C., and that this amount decreases to about 3 per cent. at 20° C.

In the same year Ohtani and Hemmi³ reported a solubility of 4.8 per cent. copper at 520° C., 2.6 per cent. at 460° C. and 1.5 per cent. at 420° C.

* Metallurgist, Research Bureau, Aluminum Co. of America.

† Assistant Metallurgist, Research Bureau, Aluminum Co. of America.

¹ Constitution and Metallography of Aluminum and Its Light Alloys with Copper and Magnesium. *Scientific Paper* No. 337, U. S. Bur. Standards.

² Rosenhain, Archbutt and Hanson: Eleventh Report to Alloys Research Committee of Inst. of Mech. Engrs. (1921) 200.

³ *Jnl. Chemical Industries (Japan)* (1921) **24**, 1353. *Chem. Abs.*, **16** (1922) 3299.

The latter investigation was carried out by means of electrical resistance measurements, whereas the former employed microscopic examination.

The aluminum used in these investigations was probably of the highest purity then obtainable. Since that time, however, aluminum of much higher purity has recently become available through the development, by the Aluminum Co. of America, of a new process for electrolytically refining aluminum.⁴ The present investigation was undertaken because of discrepancies in the previously published results and in line with the policy of the Aluminum Co. of America⁵ to establish the metallography and constitution of aluminum alloys free from the contaminating impurities which hampered earlier investigators. This work comprised the rechecking of the aluminum-CuAl₂ eutectic temperature and concentration and the locating of the solidus curve, as well as the microscopic determination of the solid solubility of copper in aluminum from the eutectic temperature to 200° C. Painstaking metallographic preparation and much longer annealing periods than had been previously reported have resulted in the locating of a curve of solid solubility which is in fair agreement with the results of the National Physical Laboratory, at the eutectic temperature, and with those of Merica and his associates at low temperatures. However, it is of strikingly different shape from either and shows a much greater decrease in solubility from the eutectic temperature to 200° C. and below.

MATERIALS

The aluminum used in most of the cast specimens was of the following analysis: Cu 0.022 per cent., Fe 0.022 per cent., Si 0.039 per cent., Al, by difference, 99.917 per cent. Electrolytic copper of 99.77 per cent. purity was used. The forged alloys were prepared under the supervision of R. S. Archer, and were of the same order of purity. As a check on certain observations, some specimens were made from aluminum and copper of extreme purity. The analysis of the aluminum follows: Si 0.007 per cent., Fe 0.009 per cent., Cu 0.007 per cent., Ti 0.001 per cent., other impurities nil, Al (by difference) 99.976 per cent. The copper was obtained in the form of foil from J. T. Baker Co., who gave the following lot analysis: Fe 0.003 per cent., Sb, Sn and Pb none.

PREPARATION OF ALLOYS

In order to avoid contamination of the aluminum, crucibles machined from Acheson graphite and stirring rods of the same material were

⁴ F. C. Frary: Electrolytic Refining of Aluminum. *Trans.*, Amer. Electrochem. Soc. (1925) **47**, 259.

⁵ E. H. Dix, Jr.: A Note on the Microstructure of Aluminum-iron Alloys of High Purity. Amer. Soc. for Testing Materials (1925). (First paper of this nature.)

employed. The melting was accomplished in a small electric crucible furnace, which offered excellent temperature control. The cast alloys upon which most of the determinations were based were prepared by melting down the pure aluminum and then adding a 54 per cent. copper hardener to make 500 grams of alloy of the desired composition. The melt was stirred and poured at an average temperature of 750° C. The earlier alloys were cast in a cold graphite mold, giving cylinders 2½ in. high by ¾ in. in diameter from which specimens were cut and the circular cross-section prepared for microscopic examination.

Since some segregation was occasionally observed in the specimens so cast, it seemed desirable to devise a more satisfactory method. A mold was designed which consisted of a large block of cast iron into which were cut two channels ½ in. wide by ⅝ in. deep by 9 in. long, connected to a pouring basin in such manner as to allow rapid pouring. This gave specimens of rectangular cross-section which had been very rapidly chilled and, therefore, showed a fine, uniform structure while the amount of segregation due to slight piping in the upper surface was approximately the same along the entire length of the bar. Annealing apparently removed this slight lack of homogeneity so that cross-sections cut from different parts of the bar presented a satisfactory degree of uniformity. A thin plate sample for chemical analysis was obtained from a cold iron mold from each melt.

COOLING CURVES

To check the freezing point of the eutectic a number of cooling curves were run on 200-gm. samples, which were prepared from the aluminum of 99.917 per cent. purity. A small graphite crucible and protecting tube, similar to that recommended by the Bureau of Standards, were employed.⁶ A 0.5 mm. platinum, platinum-rhodium couple, with its insulation, was inserted in a pyrex tube to protect it from contamination by the graphite. A Hoskins electric crucible furnace 4 in. in diameter by 6 in. deep was employed and the rate of cooling regulated by adjusting the furnace resistance to give a drop of 1° C. per minute at about 100° C. above the eutectic temperature. The couple was calibrated frequently against the freezing points of Bureau of Standards samples of zinc and aluminum.

THERMAL TREATMENT FOR SOLID SOLUBILITY

In order to obtain the solid solubility of copper in aluminum at any temperature up to the eutectic temperature it was necessary to put the specimen in equilibrium at that temperature and then quench rapidly

⁶ *Tech. Paper* No. 170, U. S. Bur. Standards 193, Fig. 123.

in order to retain the structure for examination under the microscope. The presence of free CuAl_2 in the microstructure would then indicate that this particular percentage of copper was in excess of the solubility limit at the quenching temperature employed.

It is evident that because of the number of specimens involved and the length of time required for each anneal, some means of treating a number at once would be required. A Hoskins electric muffle furnace $7\frac{3}{8}$ in. wide by 5 in. high by $12\frac{1}{2}$ in. long, equipped with a two-point Leeds & Northrup recorder controller, was the most convenient furnace available. In order to damp out fluctuations in temperature due to the power being thrown on and off by the controller mechanism and to insure equal uniformity of temperature for the specimens, the mass of an aluminum block 10 in. by 6 in. by 4 in. was employed. Six holes $1\frac{3}{8}$ in. in diameter arranged in two horizontal rows and extending to within about 2 in. of the back, were drilled in the front of the block. Into these holes were inserted close-fitting tubes closed at the front end with plugs about 2 in. long, which were flush with the front of the block when the tubes were in place, except for a small projecting lug to facilitate handling. Each tube, therefore, formed an annealing chamber $\frac{7}{8}$ in. in diameter by 6 in. long. A tube could be quickly withdrawn from the block and all of the specimens quenched in a very rapid and satisfactory manner without disturbing the remainder of the specimens. Thus the specimens which were to be quenched at one temperature were loaded in a single tube and quenched at the same rate after exactly the same annealing treatment. Since a tube would accommodate as many as 15 specimens and there were six tubes, it would be possible by one anneal to obtain 15 points, if necessary, at each of six temperatures. This method has proved particularly convenient in mapping out an unknown field.

The block rested on four legs and was placed centrally in the furnace. Chromel-alumel couples were used, one of which was inserted in a hole in the back of the block and the junction pinned tightly at a point very close to the center of the block. This couple was used to record any possible variation in the block temperature. Several times daily it was connected to a precision potentiometer to obtain an actual temperature reading. The control couple was fastened midway between the top of the block and the roof of the furnace. Thus, while the fluctuations in the furnace atmosphere, due to the throwing on and off of the power, as recorded by the control couple, might be from 8 to 12°C ., yet, due to the mass of the block, the fluctuations in its temperature were less than 1°C . A careful survey was made by means of small diameter iron-constantan couples peened in blocks inserted in different parts of the annealing chambers and it was found that no point in the chambers varied more than 3°C . from the temperature as indicated by the couple fastened in the center of the block.

Annealing Methods

In order to insure equilibrium in the alloys, an annealing period of from one week to 11 days at close to the eutectic temperature was employed. After this time the first tube of specimens was withdrawn and the specimens rapidly quenched. The block was then allowed to cool very slowly to the next quenching temperature and held for a period and the second tube quenched, and so on until the desired temperature range had been covered. The rate of cooling from the annealing temperature, which would insure equilibrium at temperatures down to 300° C., was ascertained after considerable experimenting and found to be much slower at the lower temperatures. In order to supplement the results obtained from specimens cooled over this range, other specimens which had been retained as homogenous solid solutions by quenching from the annealing temperature were reheated to 300-350-400 and 450° C. and held at these temperatures long enough to insure equilibrium. Annealing was also carried out at 200° C. in an oil bath equipped with an automatic temperature controller and a Tycos recording thermometer, the specimens being left in the bath one and two weeks.

The location of the solidus line was checked by determining the highest temperature at which specimens of a given copper content could be heated without showing signs of incipient fusion when examined under the microscope after quenching.

In the heat treatment of specimens for the preliminary location of the line, a copper block and tubes were substituted for the aluminum, because of the higher temperatures involved. The temperature of the specimens before quenching was taken as that indicated by the chromel-alumel couple fastened in the center of the block. For the final determinations, the quenching temperature was obtained by peening an iron-constantan couple into the small hole drilled in the individual specimens. The iron-constantan couples were calibrated against the freezing points of pure metals before and after the determination. The effect of rapidly quenching the couples in water from temperatures in the neighborhood of 600° C. was found to be slight. The specimens used in these determinations were annealed for a period sufficient to insure equilibrium at just under the eutectic temperature and then slowly heated to the desired quenching temperature and held for $\frac{1}{2}$ hr. The variation in temperature during the half-hour period was not more than 1° C., the highest point reached during this period being taken as the annealing temperature. A precision potentiometer was used with the iron-constantan couples.

METALLOGRAPHIC EXAMINATION

Specimens for metallographic examination were carefully polished, employing the best methods available, and yet sufficient surface flow was

produced to obscure very small particles of constituents and tiny melted areas. Therefore, it was found necessary to etch in some manner to remove the surface flow. Even the most delicate etching seems to develop polishing defects which were previously unsuspected. For this work it was found most satisfactory to swab the specimens with a soft cotton swab saturated with $\frac{1}{2}$ per cent. aqueous HF solution. This satisfactorily removed the surface flow, revealing the CuAl_2 as clear, nearly colorless particles with black boundaries. This method of etching was found to be much more satisfactory than employing an etching reagent which darkened or blackened the CuAl_2 , for in this case it would be impossible to differentiate between small particles of the constituent and black specks left in polishing. However, with very fine particles of CuAl_2 , the boundary effect becomes so pronounced as to give the entire particle a black appearance, and hence makes the exact determination a question requiring considerable experience and judgment. Small particles of the iron constituent, probably due to both the silicon and iron impurities, were generally colored by the $\frac{1}{2}$ per cent. HF.

THE COMPOUND CuAl_2

The single aluminum-copper constituent found in the high aluminum alloys is now generally recognized as CuAl_2 . The micrograph of Fig. 1b

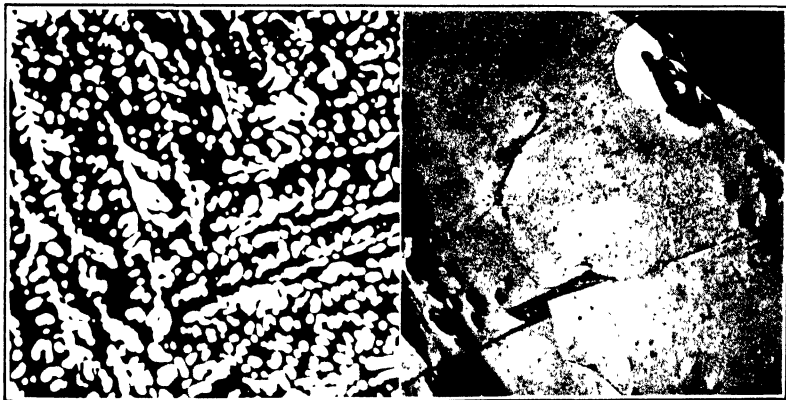


Fig. 1a. $\times 100$

Fig. 1b. $\times 100$

Fig. 1a.—ALUMINUM-COPPER ALLOY (58.89 PER CENT. CU). CHILL CAST IN GRAPHITE MOLD. ETCHED 30 SEC. IMMERSION IN NaOH . SHOWS WHITE CRYSTALS OF η CONSTITUENT IN DARK BACKGROUND OF CuAl_2 .

Fig. 1b.—ALUMINUM-COPPER ALLOY CONTAINING 53.05 PER CENT. CU, CHILL CAST. ETCHED 30 SEC. IMMERSION IN NaOH . SHOWS CuAl_2 AND SMALL CRYSTAL OF η CONSTITUENT.

illustrates the appearance of this compound when just sufficient copper has been added to the aluminum to satisfy this formula. This micrograph is representative of the structure of the hardener used in the preparation of the alloys. Fig. 1a shows the structure of an alloy containing

copper in excess of this amount. The new constituent has been designated by Stockdale⁷ as the η constituent. Due to slight segregation in casting there is a small half moon of the η constituent to be noted in Fig.

FIG. 1c. $\times 500$ FIG. 1d. $\times 500$

FIG. 1c.—ALUMINUM-COPPER ALLOY (35.69 PER CENT. CU), CHILL CAST. UN-ETCHED. LARGE PRIMARY CRYSTALS OF CuAl_2 IN BACKGROUND OF ALUMINUM-EUTECTIC.

FIG. 1d.—ALUMINUM-COPPER ALLOY (33 PER CENT. CU), CAST IN HOT GRAPHITE MOLD AND SLOWLY COOLED. ETCHED 2 HR. IMMERSION IN ALCOHOLIC PICRIC ACID SOLUTION. SHOWS EUTECTIC OF CuAl_2 BLACK AND ALUMINUM WHITE.

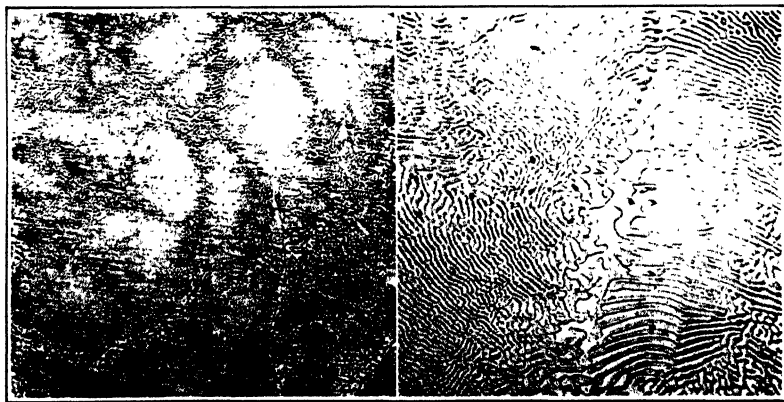
FIG. 1e. $\times 100$ FIG. 1f. $\times 500$

FIG. 1e.—SLOWLY COOLED 200-GM. SAMPLE OF ALUMINUM-COPPER (33 PER CENT. CU). ETCHED 0.5 PER CENT. HF. ILLUSTRATES AREA OF PRACTICALLY PURE EUTECTIC ON WHICH ANALYSIS WAS MADE.

FIG. 1f.—AREA AT CENTER OF FIG. 1a AT HIGHER MAGNIFICATION.

1b. With aluminum in excess of the compound concentration, primary particles of CuAl_2 appear in the ground mass of aluminum— CuAl_2 eutectic

⁷ Stockdale: Copper Rich Aluminum-copper Alloys. *Jnl. Inst. Metals*, **28** (1922).

as illustrated in Fig. 1c. The pure eutectic structure etched to blacken the CuAl_2 is shown in Fig. 1d.

The eutectic concentration is now generally considered to be close to 33 per cent. copper. This was confirmed by chemical analyses of the central area of a 200-gm. sample of 33 per cent. aluminum-copper alloy which was melted down in a graphite crucible and stirred, in order to avoid segregation, until solidification began, a very slow rate of cooling being used to avoid undercooling. The entire vertical cross section was prepared for microscopic examination. It showed the upper central area

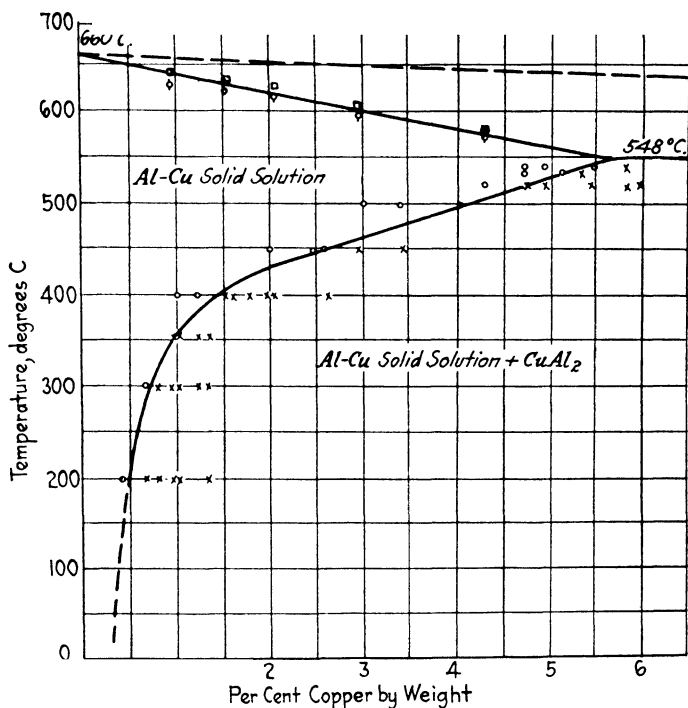


FIG. 2.—A MODIFIED DIAGRAM OF ALUMINUM END OF ALUMINUM-COPPER SYSTEM.

to be pure eutectic as illustrated in Figs. 1e and 1f. This area was marked out and two sets of drillings taken. These were analyzed and found to contain 33.32 and 32.79 per cent. copper.

THE MODIFIED DIAGRAM

From the results of this investigation, a modified diagram of the aluminum end of the aluminum-copper system is presented in Fig. 2.

THE EUTECTIC HORIZONTAL

The eutectic horizontal has been drawn at 548°C. This is in agreement with the temperature previously determined by C. S. Taylor and

reported by Archer and Jeffries.⁸ The determinations made in this investigation on aluminum alloys of various copper concentrations follow:

M No.	Per Cent. Copper	Eutectic Temp. °C.
1150	33	548.5
677	12.98	548.2
678	8.01	547.6
1183	6.74	546.9
1184	6.25	547.0
680	5.82	546.2
681	5.47	545.5

The temperatures obtained on the higher copper concentrations, particularly the eutectic alloy, give a more reliable indication of the eutectic temperature than those obtained from the lower copper concentrations. A marked eutectic arrest was found with a copper content of 5.47 per cent., which is just slightly less than the copper solubility at the eutectic temperature. However, microscopic examination of a vertical section through a 200-gm. cooling curve ingot showed that considerable segregation had taken place and the material surrounding the couple appeared to have a copper content of approximately 8 per cent.

THE SOLIDUS CURVE

The solidus curve has been drawn as a straight line from the melting point of pure aluminum of 660° C.⁹ to intersect the eutectic horizontal at 5.65 per cent. copper. The line passes between two points determined for the alloy of 2.95 per cent. copper at temperatures of 600 and 603° C., respectively. No evidence of melting was observed in the specimen quenched from the lower temperature, whereas abundant boundary melting was observed in the specimen quenched from the higher temperature. The straight line is also in satisfactory agreement with the determinations made on the alloy of 4.29 per cent. copper. Some difficulty was, however, experienced in connection with the examination of the specimens of the low copper percentages. This was because some melting appeared to take place at much lower temperatures than the temperature at which the aluminum-copper solid solution gave indications of definite melting at the grain boundaries. For instance, in the alloy containing 2.07 per cent. copper, a specimen quenched from as low as 609° C. showed some dark rosettes and crescent-shaped particles of unidentified constituent which had not been observed previously and which seemed to increase in

⁸ New Developments in High Strength Aluminum Alloys. *Trans.* (1925) Feb.

⁹ J. D. Edwards: Properties of Pure Aluminum. *Amer. Electrochem. Soc.* (1925) Apr.

FIG. 3a. $\times 1500$ FIG. 3b $\times 100$

FIG. 3a.—FORGED ALUMINUM-COPPER ALLOY (Cu 2.95 PER CENT), ANNEALED FOR 48 HR. AT 540°C . AND THEN HEATED TO 603°C . FOR $\frac{1}{2}$ HR. AND QUENCHED. ETCHED 0.5 PER CENT. HF. SHOWS JUNCTION OF THREE GRAINS ILLUSTRATING FIRST INDICATION OF MELTING, AS SHOWN BY BLACK, Y-SHAPED CAVITY IN CENTER.

FIG. 3b.—FORGED ALUMINUM-COPPER ALLOY (Cu 4.29 PER CENT.), ANNEALED FOR 48 HR. AT 540°C . QUENCHED AND REHEATED TO 584°C ., AND HELD FOR $\frac{1}{2}$ HR. AND QUENCHED. ETCHED 0.5 PER CENT. HF. SHOWS AREA OF SPECIMEN WHERE MELTING HAS BEEN PRONOUNCED ALONG GRAIN BOUNDARY.

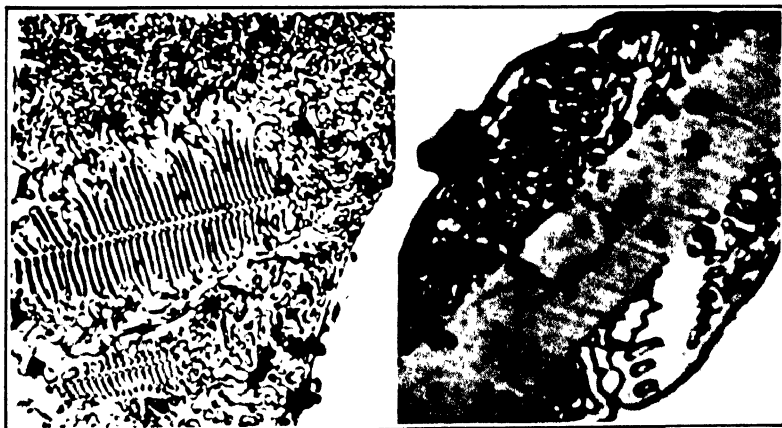
FIG. 3c. $\times 1500$ FIG. 3d. $\times 3000$

FIG. 3c.—SHOWS MELTED AREA IN GRAIN BOUNDARY AT LOWER LEFT-HAND CORNER OF FIG. 3b AT HIGHER MAGNIFICATION.

FIG. 3d.—SHOWS MELTED AREA SURROUNDING NEEDLE OF IRON CONSTITUENT, SHOWN IN UPPER LEFT-HAND CORNER OF FIG. 3b.

quantity as the temperature was raised. They were found in fairly large quantities in the specimen quenched from 618° C., but no direct evidence of solid solution melting at the grain boundaries could be observed. Specimens quenched from fully 10° C. higher showed only slight evidence of melting at the grain boundaries. All of this would seem to indicate that the lower temperature effects noted were due to some cause other than

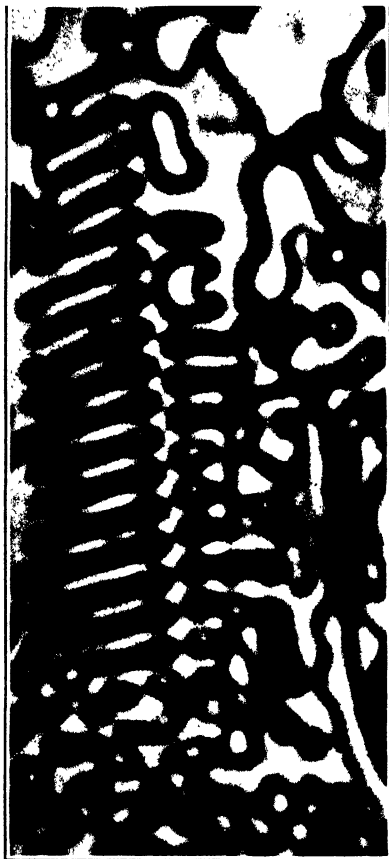


FIG. 3e. $\times 8000$

FIG. 3e.—SHOWS REGULAR STRUCTURE IN LOWER PART OF FIG. 3c AT HIGHER MAGNIFICATION. THE CuAl_2 IS SHOWN IN HALF-TONE IN RELIEF ABOVE THE LIGHT ALUMINUM.

aluminum-copper solid solution melting. It was, therefore, felt that the straight line drawn as shown on the diagram represented the true conditions more nearly than either a convex or a concave curve.

First Evidence of Melting

The first evidence of solid solution melting was found to be minute cavities formed at the junction of three grains, as illustrated in Fig. 3a.

Fig. 3b shows pronounced melting along the grain boundaries in a forged specimen of 4.29 per cent. copper, which was heated to just 8° C. above the solidus curve, as drawn in the diagram of Fig. 2. The large, black area in the grain boundary at the lower left of this micrograph is shown at much higher magnification in Fig. 3c, which clearly shows the effect of rapid cooling caused by the quenching of the specimen when this area consisted of a pool of liquid of very close to eutectic concentration. Fig. 3e shows the regular formation in the lower left of Fig. 3c at much higher magnification and illustrates very clearly the CuAl_2 , which appears in half-tone and forms the greater area, in contrast to the clear white of the aluminum solid solution. Owing to the difference in hardness between the CuAl_2 and aluminum, the former stands in relief and the boundaries between it and the aluminum overlap so as to give the appearance of a third dark constituent, but a close examination of Fig. 3e will show that this is not true, and that only the constituents previously noted are present.

The effect of even small amounts of impurities as influencing the melting outside of the grain boundaries is illustrated in Fig. 3d, which shows the small area in the upper left of Fig. 3b at much higher magnification. The gray needle of the iron impurity has evidently produced melting of the aluminum solid solution around it, which has resolidified on quenching, in the characteristic aluminum- CuAl_2 eutectic structure. In Figs. 3c and 3d there will be noted irregular black areas which are different from the boundary effect mentioned in connection with Fig. 3e. This seems to be characteristic of these alloys when heated to high temperatures, and may be partly responsible for the difficulties encountered in connection with the examination of the alloys of lower copper concentration.

THE SOLUBILITY RELATIONS

The solubility curve of copper in aluminum shows a very rapid decrease in solubility with falling temperature from slightly over 5½ per cent. copper at 548° C. to about 2 per cent. at 430° C., the curve being practically straight in this range. From this temperature to about 300° C. there is a marked slowing up in the rate of decrease, and from 300° C. to normal temperatures the rate of change is comparatively slight, although no data were obtained below 200° C. The knee of the curve occurs at about 385° C. and a copper concentration of 1¼ per cent. The solubility at normal temperatures is certainly less than ½ per cent. There are many more determinations to the right of this curve than to the left, which is due to the fact that previously published work indicated a much higher solubility, particularly at the low temperatures, than was shown by this investigation.

Very careful preparation of specimens and laborious microscopic examination, coupled with considerable judgment, was necessary in

determining the final position of the curve, for even with the pure metal used in this investigation, there were sufficient particles of the iron or other constituent present to sometimes result in confusion. The differentiation between CuAl_2 and other constituents is a very simple matter in particles of relatively large size. However, as the particle size decreases the differentiation becomes increasingly difficult and in specimens containing very little of any hard constituent polishing defects introduce another source of error. However, it is believed that by the methods employed a difference in solubility of $\frac{1}{4}$ per cent. is readily detected and that because of the large number of points the curve is probably correct to even less than this amount.

Most Interesting Results of Investigation

The annealing for several weeks at 200°C. of specimens previously brought to equilibrium at higher temperatures yielded the most interest-

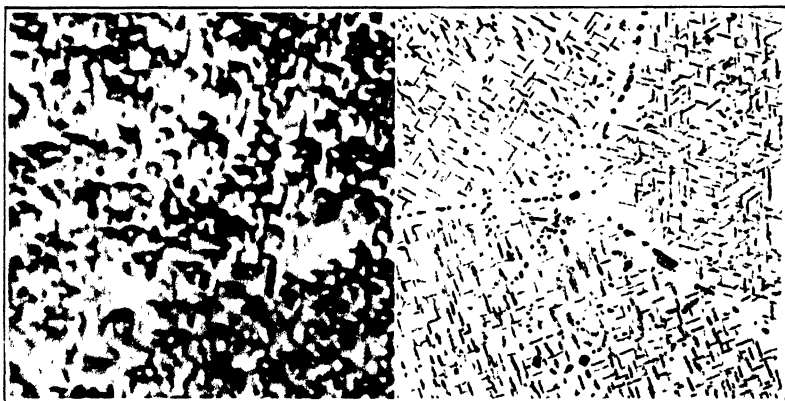


FIG. 4a. $\times 3000$

FIG. 4b. $\times 500$

FIG. 4a.—CHILL CAST ALUMINUM-COPPER ALLOY (Cu 1.60 PER CENT.). ANNEALED FOR ONE WEEK AT 520°C. , AND THEN SLOWLY COOLED TO ROOM TEMPERATURE. REHEATED FOR ONE WEEK AT 200°C. , QUENCHED AND ANNEALED ANOTHER WEEK AT 200°C. AND QUENCHED. ETCHED 1 PER CENT. HF. THIS MICROGRAPH ILLUSTRATES EFFECT PRODUCED BY COALESCENCE OF PRECIPITATE TO SIZE WHICH IS PROBABLY STILL SUB-MICROSCOPIC.

FIG. 4b.—SAME ALLOY AS FIG. 4a. ANNEALED FOR 11 DAYS AT 540°C. , QUENCHED IN COLD WATER AND REHEATED TO 300°C. FOR $101\frac{1}{2}$ HR. ETCHED 0.5 PER CENT. HF (LIGHT). SHOWS JUNCTION OF THREE GRAINS REVEALING FINE, NEEDLE-LIKE PRECIPITATE OF CuAl_2 AND PARTICLES OF CuAl_2 (LIGHT) AND IRON CONSTITUENT (DARK) IN GRAIN BOUNDARIES.

ing results of the investigation. In the specimens containing copper in excess of the solubility limit, at this temperature, discrete particles of CuAl_2 were found in the grain boundaries and in addition a peculiar mottled appearance was noted in the matrix. This condition in an alloy of 1.60 per cent. copper, slowly cooled from equilibrium at 520°C. , is illustrated in Fig. 4a. It was found to be absolutely impossible to

FIG. 4c. $\times 100$ FIG. 4d. $\times 1500$

FIG. 4c.—ALUMINUM-COPPER ALLOY (Cu 0.70 PER CENT.) CHILL CAST IN IRON MOLD AND ANNEALED FOR 11 DAYS AT 540°C . QUENCHED AND REHEATED AT 200°C . FOR TWO WEEKS. ETCHED 0.5 PER CENT HF (HEAVY). SHOWS GRAIN BOUNDARIES AND PRECIPITATE.

FIG. 4d.—SAME SPECIMEN AS 4c. ETCHED 0.5 PER CENT. HF. SHOWS JUNCTION OF THREE GRAINS WITH LARGE STRINGER OF CuAl_2 AND FINE NEEDLE-LIKE PRECIPITATE OF CuAl_2 .

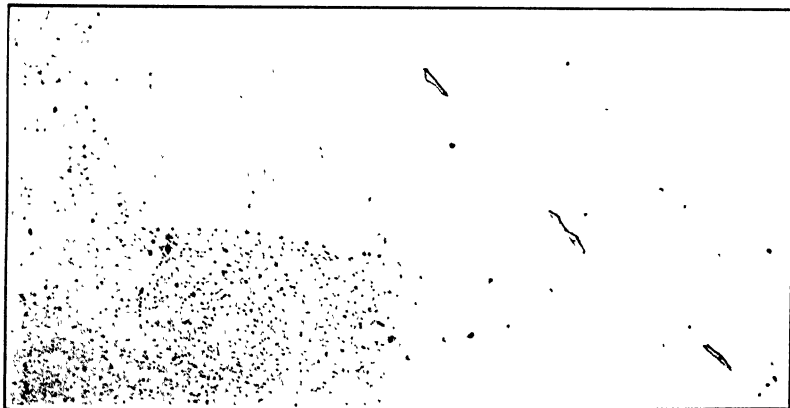
FIG. 4e. $\times 100$ FIG. 4f. $\times 500$

FIG. 4e.—FORGED ALUMINUM-COPPER ALLOY (Cu 0.97 PER CENT.), ANNEALED FOR 11 DAYS AT 540°C . QUENCHED AND REHEATED TO 300°C . FOR 120 HR. AND QUENCHED. ETCHED 0.5 PER CENT. HF (LIGHT). SHOWS AVERAGE STRUCTURE ILLUSTRATING CuAl_2 PARTICLES IN GRAIN BOUNDARIES AND PRECIPITATE IN CERTAIN GRAINS WHICH IS UNDOUBTEDLY EXAGGERATED IN SIZE BY THE ETCH.

FIG. 4f.—ALUMINUM-COPPER ALLOY (Cu 0.83 PER CENT.) CHILL CAST IN IRON MOLD. ANNEALED FOR 11 DAYS AT 540°C ., THEN SLOWLY COOLED AS FOLLOWS: 450°C . IN 48 HR., 400°C . IN 168 HR., 300°C . IN 288 HR., AND THEN QUENCHED. SHOWS THREE PARTICLES OF CuAl_2 ARRANGED ALONG GRAIN BOUNDARIES.

definitely resolve particles in this matrix, even at the highest magnifications, but there was always a suggestion of uniformly oriented figures which indicated that a definite arrangement of a sub-microscopic precipitate was responsible for these etching characteristics. It was felt that if such were the case it should be possible to cause a further coalescence of these particles by heating to a higher temperature. This proved to be true.

Fig. 4b shows the effect of reheating a specimen of the same alloy at 300° C. for 101½ hr., subsequent to quenching from equilibrium at 540° C. Particles of CuAl₂ of appreciable size will be found in the grain boundaries, together with smaller dark-etching particles of the constituent formed by the impurities iron and silicon. Figs. 4c and d illustrate a similar precipitate in an alloy of 0.70 per cent. copper chill cast in an iron mold and annealed for 11 days at 540° C., quenched and reheated to 200° C. for two weeks. Definite particles of constituent will be observed in the grain boundaries and the matrix within the grains has a mottled appearance at low magnification which is shown at higher magnification to be due to a fine precipitate. In the upper grain, discrete particles will be observed which are probably greatly exaggerated by the etching. In the grain to the left there will be observed numerous paths extending in an irregular manner across the grain. These are areas of clear solid solution, the precipitate having apparently coalesced into particles of visible size, such as may be noted in the prominent path extending downward from the boundary of the two lower grains. The same phenomenon was observed at the grain boundaries (see Figs. 4b, d, and e). The large, dark particle in the center of Fig. 4d is CuAl₂ which appears dark because the focus was concentrated on the particles of precipitate shown in the matrix. Fig. 4e illustrates the structure of an aluminum-copper alloy of 0.97 per cent. copper, which was annealed for 11 days at 540° C., quenched and reheated 120 hr. at 300° C. and quenched.

In the micrograph of Fig. 4f are shown three particles of CuAl₂, arranged along the grain boundary of an alloy of 0.83 per cent. copper, chill cast in an iron mold and annealed for 11 days at 540° C. and then slowly cooled as follows: 48 hr. to 450° C., 168 hr. to 400° C., 288 hr. to 300° C. and then quenched. This concentration is just slightly to the right of the solubility curve at 300° C. and only a few such particles were observable in this specimen. It should be noted that the aluminum solid solution appears perfectly clear and has no resemblance to the mottled appearance found in the other micrographs of Fig. 4, all of which illustrate alloys which have been reheated after having been cooled to room temperature.

Structure of a Pure Aluminum-copper Alloy

It may now be of interest to study the structure of a pure aluminum-copper alloy in various conditions. The micrographs of Fig. 5 illustrate

structures of an alloy containing 4.05 per cent. copper, which roughly approximates the amount used in commercial strong aluminum alloys. Thus, Fig. 5a shows the structure of this alloy after casting in a hot graphite mold and slowly cooling. This is representative of the structure obtained in an ordinary sand casting of this composition. Reference to the diagram of Fig. 2 will show that had this alloy solidified at a rate slow enough to follow equilibrium conditions, the solid alloy at, say 550°C ., should consist of grains of the aluminum solid solution with no excess CuAl_2 . However, owing to selective freezing at a rate too rapid to allow the crystals first formed to reach equilibrium, the last liquid remaining in the interstices between the primary aluminum dendrites had become sufficiently concentrated so that a considerable amount of eutectic was formed as a fairly continuous network.

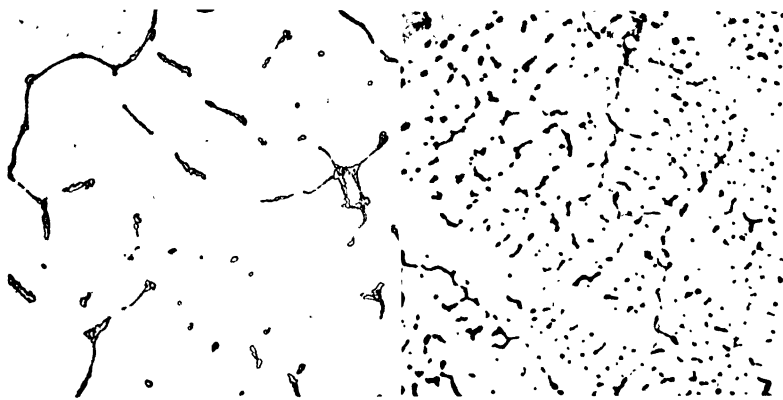
FIG. 5a. $\times 100$ FIG. 5b. $\times 100$

FIG. 5a.—ALUMINUM-COPPER ALLOY (CU 4.05 PER CENT.) VERY SLOWLY SOLIDIFIED AFTER CASTING IN HOT GRAPHITE MOLD. ETCHED 0.5 PER CENT. HF (LIGHT). SHOWS AVERAGE AREA ILLUSTRATING FORMATION OF CuAl_2 NETWORK.

FIG. 5b.—SAME ALLOY CAST IN COLD GRAPHITE MOLD. ETCHED 0.5 PER CENT. HF (LIGHT). SHOWS AVERAGE AREA OF SPECIMEN ILLUSTRATING FINE NETWORK OF CuAl_2 , WHICH APPEARS BLACK BECAUSE OF BOUNDARY EFFECT DUE TO LACEWORK STRUCTURE OF PARTICLES.

Fig. 5b shows the same alloy cast as a cylinder $\frac{3}{4}$ in. in diameter by 2 in. long in a cold graphite mold. This has produced a much more rapid rate of solidification, giving a much finer structure and smaller particles of CuAl_2 . Although this specimen was etched in the same manner as that shown in previous micrograph, yet the CuAl_2 appears much darker by comparison. This is because of the increased boundary effect, particularly since the particles of CuAl_2 are not solid, as they appear at this magnification, but are actually in a lacey formation. Fig. 5c shows a cross-section of a specimen cut from the bar of Fig. 5b, annealed for one week at 540°C . and then slowly cooled through a period of 120 hr. to room temperature. The annealing at 540°C . has caused all of

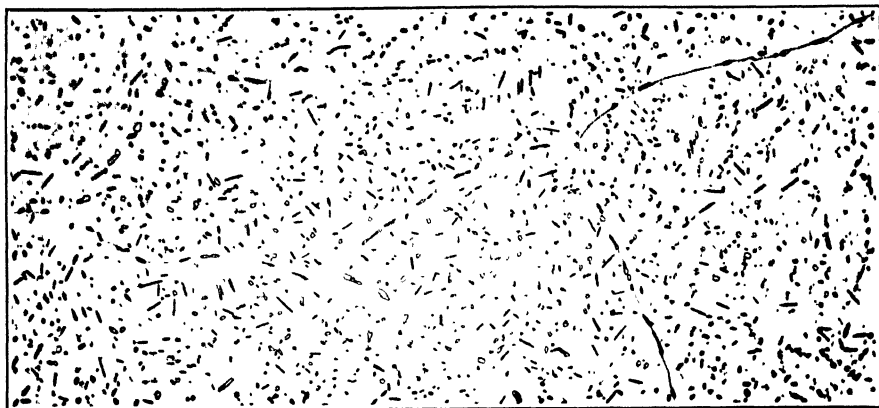
FIG. 5c. $\times 100$

FIG. 5c.—SPECIMEN CUT FROM BAR OF FIG. 5b, ANNEALED FOR ONE WEEK AT 540°C . AND THEN SLOWLY COOLED THROUGH A PERIOD OF 120 HR. TO ROOM TEMPERATURE. ETCHED 0.5 PER CENT. HF. SHOWS AVERAGE STRUCTURE OF SPECIMEN CONTAINING REGULAR PARTICLES OF CuAl_2 PRECIPITATE ARRANGED ALONG GRAIN BOUNDARIES AND UNIFORMLY DISTRIBUTED THROUGHOUT MATRIX.

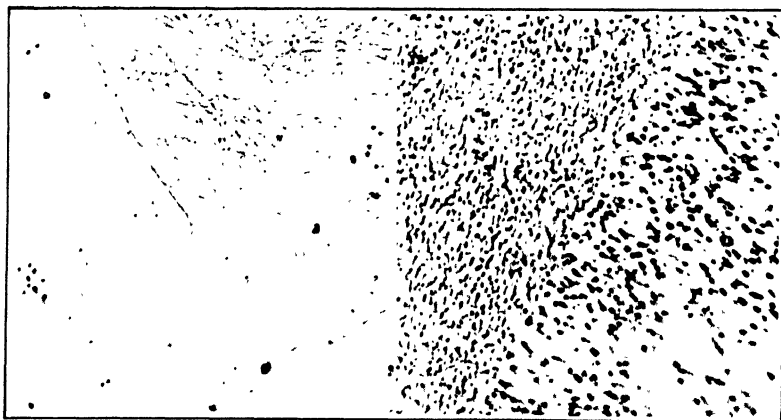
FIG. 5d. $\times 500$ FIG. 5e. $\times 1500$

FIG. 5d.—SPECIMEN TAKEN FROM SAME BAR AS FIG. 5b, ANNEALED FOR ONE WEEK AT 540°C . AND SLOWLY COOLED THROUGH PERIOD OF 24 HR. TO 500°C ., AND THEN QUENCHED. ETCHED 0.5 PER CENT. HF. JUNCTION OF THREE GRAINS SHOWING COMPLETE SOLUBILITY OF CuAl_2 AT THIS TEMPERATURE. BLACK SPECKS ARE POLISHING DEFECTS REVEALED BY ETCH.

FIG. 5e.—SPECIMEN FROM BAR OF FIG. 5b, ANNEALED FOR 11 DAYS AT 540°C ., QUENCHED AND REHEATED FOR TWO WEEKS AT 200°C . ETCHED 0.5 PER CENT. HF. SHOWS PARTICLES OF COALESCESED CuAl_2 PRECIPITATE DIFFERENTLY ORIENTED IN TWO GRAINS.

the copper to go into solution and the slow cooling from this temperature has caused the precipitation of these large particles according to the solid solubility curve of Fig. 2. It will be observed that particles of CuAl_2 are arranged along the grain boundaries and are also uniformly scattered throughout the matrix. The general tendency of this precipitate is towards very regular and angular particles having definite orientations.

Fig. 5d shows a section of the same specimen as Fig. 5b, which had been annealed for a week at 540°C ., slowly cooled to 500°C . and then quenched. All of the CuAl_2 has disappeared from the microstructure and the micrograph, therefore, shows three grains of homogeneous alloy. The black specks are due to polishing defects brought out by the etching. A portion of this same specimen after a further annealing for two weeks at 200°C ., showed the structure illustrated in Fig. 5e. This shows portions of two grains containing a very fine precipitate of particles of CuAl_2 . The particles of precipitate seem to have formed thin plates, having a width perhaps three or four times the thickness and a length generally greater than the width. The orientation of the upper left-hand grain has been such that the polishing plane has shown the thin cross-sections of the plates, whereas the lower right-hand grain is oriented so that the flat sections of the plates are revealed, giving the appearance of coarser and less numerous particles than in the former grain.

Hardness Values

The hardness values of the structures illustrated in the micrographs of Fig. 5 are of interest. The slowly cooled specimen had a Brinell hardness, using a 125-kg. load and a 5-mm. ball, of 39 and the chill cast specimen a hardness of 44, whereas the same specimen after slow cooling from equilibrium at 540°C . had a hardness of only 30.4. The same specimen quenched from equilibrium at 540°C . and aged at room temperature for approximately one year, showed a Brinell hardness of 65.8. Subsequent aging for nine days at 200°C . gave a Brinell hardness of 68.0.

Precipitation Theory

The precipitates shown in Figs. 5e and 4a to 4e, inclusive, are of great interest in connection with the precipitation theory, as proposed by Merica, Waltenberg and Scott.¹⁰ The statement made by these authors may not be out of place at this point: "A theory of the mechanism of hardening of duralumin during aging after quenching from high temperatures was developed, which is based on the decreasing solubility of the compound CuAl_2 in solid solution in aluminum with decreasing temperatures from 520°C . to ordinary temperatures. It is believed that the precipitation of excess CuAl_2 which is suppressed by quenching proceeds

¹⁰ Heat Treatment of Duralumin. *Trans.* (1919).

during aging, the precipitation taking place in very highly dispersed form. The hardening is due to the formation of this highly dispersed precipitate."

This conclusion was based largely on indirect evidence. These authors were unable to obtain evidence in the form of a visible precipitate to confirm their deductions, even after reheating 20 hr. at 300° C. It is now shown that this precipitate which they considered as being present in sub-microscopic form in normal quenched and aged duralumin can be produced in a size visible under the modern microscope, at least in pure aluminum-copper alloys, by aging for several weeks at 200° C. Previously, Mr. Thomas Doran¹¹ had discovered a precipitate in specimens reheated within the annealing range. He observed a very fine and even dispersion of CuAl_2 in a specimen containing 5.45 per cent. copper, which had been quenched from 540° C. and reheated for $\frac{1}{2}$ hr. at 371° C. He also observed this condition in a specimen reheated to 343° C.

Slip Interference Theory

The very regular orientation of the precipitate after it has coalesced to a size visible under the microscope also lends additional weight to the slip interference theory of Jeffries and Archer,¹² who proposed that the small particles of this hard and inherently strong constituent should be considered to act as keys on the crystallographic planes of easy slip of the matrix, thus opposing or interfering with the relative movement of crystal fragments along these planes.

When Merica and his associates first introduced the precipitation theory their diagram showed a change in solubility of copper in aluminum, from the heat treating temperature to room temperature, of something over 3 per cent. The diagram given by the National Physical Laboratory several years later showed a difference in solubility of only 2 per cent. In discussing high strength aluminum alloys, Jeffries and Archer¹² offered a diagram which showed a much greater decrease in solubility with falling temperature. The exact shape of the curve had not been determined, nor had the solubility of the lower temperatures been carefully investigated at that time. The modified diagram now presented in Fig. 2 shows that the true solubility change is close to 5 per cent. and that the solubility limit at temperatures below 200° C. is less than $\frac{1}{2}$ per cent. The shape of the curve is very different from any previously offered. The results of Ohtani and Hemmi, previously mentioned, are in very satisfactory agreement with this curve. Unfortunately, this original work is not readily available in this country, the values quoted having been taken from *Chemical Abstracts* and, therefore, it has not been possible to make a more complete comparison with this work.

¹¹ Cleveland Section, Research Bureau, Aluminum Co. of America.

¹² New Developments in High Strength Aluminum Alloys. *Trans.* (1925).

Effect of Impurities in Aluminum

The effect of the impurities iron and silicon, always present in aluminum of commercial purity, on the solubility of copper has not been thoroughly investigated, but it does not seem likely that small amounts of these impurities could affect the copper solubility relations sufficiently to account for the difference between a solubility of 3 per cent. at 20° C., as given by the National Physical Laboratory, and that of approximately $\frac{1}{2}$ per cent. at 200° C., as shown by this investigation. There are several possible explanations which occur to the authors. Because of the slow reaction rate at the low temperatures, the annealing times employed by the National Physical Laboratory may not have been sufficiently long to establish equilibrium, or owing to the very small particle size of the CuAl_2 when annealed at these low temperatures and the difficulty in distinguishing these small particles from equally small particles of the iron constituent, the presence of free CuAl_2 may have been overlooked in the metallographic examination.

Having established the copper solubility relations in aluminum of high purity with some degree of certainty it will now be comparatively easy to establish the effect on these solubility relations of other elements, generally present in commercial strong alloys. It is hoped that such results will be available in the not-too-distant future.

ACKNOWLEDGMENT

In conclusion, the authors desire to acknowledge with thanks the services of A. C. Heath, Jr., J. A. Nock, Jr., and G. W. Wilcox, for assistance in the experimental work, and to express appreciation to H. V. Churchill, under whose direction the chemical analyses were made.

TABLE 1.—*Description of Alloys*

M No.	Analysis			Type of Specimen
	Cu, Per Cent.	Fe, Per Cent.	Si, Per Cent.	
1331	0.007	0 009	0 007	Ingot
360	0.022	0 022	0 039	Ingot
1332	99.99	0 0003		Foil
535	99.77			Ingot
642AR	53 05	0 06	0.02	Chill cast in cold graphite mold
679	6 54			Chill cast in cold graphite mold
680	5.82			Chill cast in cold graphite mold
681	5 47			Chill cast in cold graphite mold
682	4 73	0 03	0 02	Chill cast in cold graphite mold
683	4 05			Chill cast in cold graphite mold
684	3.44			Chill cast in cold graphite mold
685	3 01			Chill cast in cold graphite mold
686	1 97			Chill cast in cold graphite mold
687	0 98			Chill cast in cold graphite mold
688	0 47	0 04	0 03	Chill cast in cold graphite mold
711	2.61			Chill cast in cold graphite mold
712	1.60			Chill cast in cold graphite mold
713	1.25			Chill cast in cold graphite mold
769	2.47			Forged
770	2 95			Forged
771	3.43			Forged
772	3 94	0.02	0 02	Forged
773	4 29			Forged
774	4.96			Forged
775	5 45			Forged
776	5 94			Forged
847	0 97			Forged
848	1 35			Forged
849	1.53			Forged
850	1.78			Forged
851	2 07			Forged
853	1 04	0.03		Chill cast in iron mold
854	2 03	0 02		Chill cast in iron mold
855	0 83	0 02		Chill cast in iron mold
856	0 70	0 02		Chill cast in iron mold
1150	33.0			Slowly cooled
1333	2 05			Chill cast in iron mold
1334	2.18	0 010	0 009	Chill cast in iron mold
1335	2.48			Chill cast in iron mold
1336	4.75			Chill cast in iron mold
1337	5.16	0.008	0.009	Chill cast in iron mold
1338	5.35			Chill cast in iron mold

Modification and Properties of Sand-cast Aluminum-silicon Alloys

BY ROBERT S. ARCHER* AND L. W. KEMPF,* CLEVELAND, OHIO

(New York Meeting, February, 1926)

It is now well known that the structure of aluminum-silicon alloys can be refined in a rather remarkable manner, with consequent improvement of physical properties, by certain treatments applied to the molten metal shortly before casting. The differences between the treated and the untreated alloys are so marked that special terms are used to distinguish them, the untreated alloys being referred to as "normal" and the treated alloys as "modified."

The first practical method of accomplishing this result was that of A. Pacz,¹ which consists in treating the molten metal with a salt flux of which the active ingredient is sodium fluoride. The result can also be brought about, and in a more economical manner, by the addition of small quantities of metallic sodium (or potassium) to the molten alloy shortly before casting.² The action of the Pacz flux evidently consists essentially in the production of free sodium by the reaction of sodium fluoride with aluminum. The changing of a normal alloy to a modified alloy is referred to as "modification" and any process for accomplishing this result is a "modifying" process.

Modified aluminum-silicon alloys were introduced several years ago, and it has been demonstrated both in the laboratory and in commercial practice that it is no simple matter to produce castings having the maximum or nearly the maximum properties which under favorable circumstances can be obtained. The alloys are rather sensitive to small changes in chemical composition, and the modifying process must be carried out in a very particular manner to obtain the best results. Extensive experimental work has been carried out in the laboratories of the Aluminum Co. of America with the object of determining the conditions that must be observed to make these alloys of the greatest possible value. It was necessary to learn how to control the modifying process

* Research Bureau, Aluminum Co. of America.

¹ A. Pacz.: U. S. Patent No. 1387900. Applied for Feb. 13, 1920; issued Aug. 16, 1921.

² J. D. Edwards, F. C. Frary, H. V. Churchill: U. S. Patent No. 1410461. Applied for Nov. 27, 1920; issued Mar. 1, 1922.

before exact work could be done on the effects of alloy composition. It is the purpose of this paper to present the essential results of the work bearing on the control of the modifying process, and the results of the investigation of the effects of alloy composition with respect to the two important elements, silicon and iron.

CONSTITUTION OF ALUMINUM-SILICON ALLOYS

Aluminum and silicon form a simple eutectiferous system, with no chemical compounds. The melting point of pure aluminum is 660°C ., while that of silicon is taken as 1420°C . The normal eutectic alloy

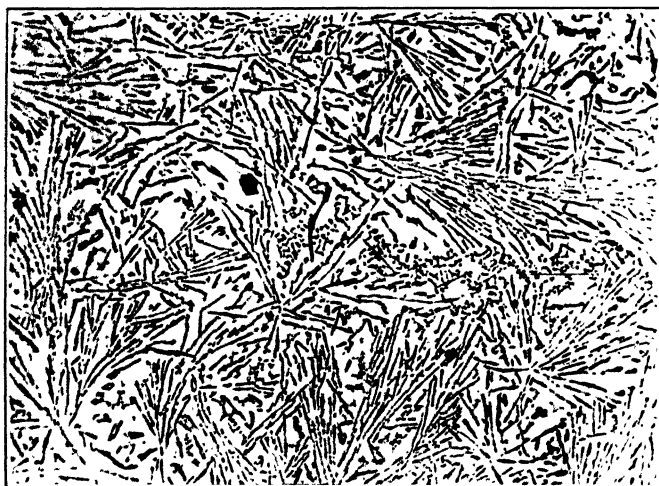


FIG. 1.—NORMAL 13.2 PER CENT. SILICON ALLOY, SAMPLE 4017, ETCHED WITH 0.5 PER CENT. HF. $\times 100$. ALUMINUM IS WHITE, SILICON BLACK, AND IRON CONSTITUENT HALFTONE. TENSILE STRENGTH 20,225 LB. PER SQ. IN.; ELONGATION 3.0 PER CENT.

contains about 11.6 per cent. silicon and melts at 577°C . Silicon is soluble in solid aluminum to the extent of about 1.5 per cent. at the eutectic temperature. This solubility does not appear to play an important part in the present discussion, and the aluminum-rich solid solution will for simplicity be referred to as "aluminum." The solubility of aluminum in solid silicon is not known but is probably very slight, and does not appear to require consideration.

THE MODIFICATION EFFECT

The binary aluminum-silicon alloys of general usefulness are those containing from about 5 to 15 per cent. silicon. Throughout this range of composition the structure can be refined and the physical properties

materially improved by the modifying process. Both the degree of improvement and the actual properties reach a maximum, however, at



2.—SAME AS FIG. 1. $\times 500$. SILICON IS BLACK, IRON CONSTITUENT IN HALF-TONE.

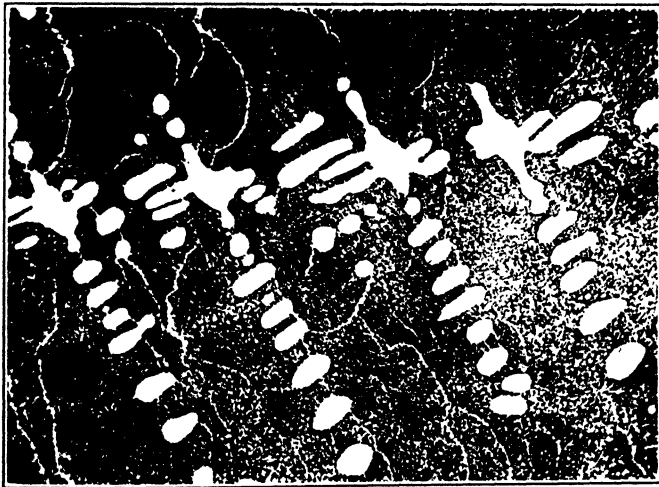


FIG. 3.—ALLOY SHOWN IN FIGS. 1 AND 2 AFTER MODIFICATION WITH SODIUM. WHITE ALUMINUM DENDRITES AND VEINS IN MATRIX OF MODIFIED EUTECTIC. ETCHED WITH 5 PER CENT. HF. $\times 100$. TENSILE STRENGTH 26,950 LB. PER SQ. IN.; ELONGATION 14.5 PER CENT.

about 13 per cent. silicon, and in commercial practice the modifying process is at present applied almost exclusively to alloys of approximately

this silicon content. The structural changes brought about by modification are well illustrated in these alloys.

Fig. 1 shows the microstructure of a normal alloy containing about 13 per cent. silicon, cast in a green-sand mold in the form of a test bar $\frac{1}{2}$ in. in diameter. The white constituent is aluminum and the dark constituent is silicon. In the normal condition, this is a hypereutectic alloy, and the primary or excess silicon is represented by particles which may be distinguished from those of the eutectic by the fact that they are usually larger and of more nearly equiaxed shape. These are surrounded by a matrix of aluminum-silicon eutectic in which the silicon occurs largely in the form of plates or needles. Fig. 2 shows the same specimen at higher magnification.



FIG. 4.—SAME AS FIG. 3. $\times 500$. ALUMINUM WHITE, SILICON BLACK. FAINT LINES OF IRON CONSTITUENT IN HALFTONE.

Fig. 3 shows the structure of the same alloy modified by the addition of sodium to the melt and cast in the same kind of a mold. There are no particles of excess silicon, but instead there are dendrites of primary aluminum (white) in a matrix (dark) of aluminum-silicon "eutectic" which is so fine that it is not resolved at this magnification. This structure is shown in greater detail in Fig. 4. The silicon particles (dark) are here seen to be very small and more or less rounded in shape.

From these micrographs it will be seen that modification involves: (1) suppression of the crystallization of primary silicon (in the case of hypereutectic alloys); (2) great refinement of the structure of the "eutectic"; and (3) shifting of the apparent "eutectic" composition toward a higher silicon content.

THEORY OF MODIFICATION

The theory of modification has been discussed in detail elsewhere,^{3, 4} and only a summary will be given here.

First, it is well to call attention to the discovery that the structural changes described can be brought about by causing the aluminum-silicon alloys to solidify rapidly, as by casting in an iron mold, without the use of sodium or any other modifying agent. In this case the phenomena are evidently due to undercooling. If the 13 per cent. silicon alloy undercooled equally with respect to both aluminum and silicon, then the solid alloy would still show primary silicon and eutectic, the undercooling merely causing refinement. The fact that primary silicon is replaced by primary aluminum shows that the crystallization of the silicon is suppressed by undercooling much more than is the crystallization of the aluminum.

Casting in a green-sand mold in sections of ordinary thickness does not cause sufficiently rapid freezing to produce modification. The sand-cast alloys can be modified by the special flux or alkali metal treatments, in which case the change is due essentially to the suppression of the crystallization of the silicon by the presence of metallic sodium in the metal at the time of solidification. The freezing point of the eutectic, normally at 577° C., is lowered by modification, temperatures as low as 564° C. having been recorded. In alloys containing more than the eutectic proportion of silicon the temperature of separation of primary silicon from the melt is lowered by the presence of sodium, and if the silicon content is not too great the crystallization of the primary silicon is entirely suppressed.⁵ On the other hand, in alloys containing less than the eutectic amount of silicon, the temperature of separation of the primary aluminum does not seem to be appreciably affected by the presence of sodium.

The mechanism by which a small quantity of sodium (less than 0.10 per cent.) suppresses the crystallization of silicon is still a matter of speculation. Mention may be made of two views developed by the Research staff of the Aluminum Co. of America. These may be referred to as the "colloid" theory and the "adsorption" theory. According to the first, the sodium, which is only slightly soluble in molten aluminum, is present in the liquid aluminum-silicon alloy at the time of solidification in the form of vast numbers of liquid particles of colloidal

³ J. D. Edwards and R. S. Archer: The New Aluminum-silicon Alloys. *Chem & Met. Engng.* (1924) **31**, 504.

⁴ Zay Jeffries and R. S. Archer: The Science of Metals, New York, McGraw-Hill Book Co., Inc., 1924.

⁵ These observations are based on cooling curves and microscopic examinations, methods which are limited in their sensitivity. It is probable that nuclei of primary silicon actually form at or near the normal temperatures, and that the apparent "suppression" is merely a retardation of crystal growth.

size. These particles are considered as mechanically obstructing the growth of the silicon crystals in much the same way that particles of thoria obstruct grain growth in solid tungsten.⁶ According to the other view, the growth of the silicon crystals is hindered by the adsorption of sodium, the silicon particles becoming partly or completely covered with films of sodium of atomic thickness.

It is quite logical that the development of the silicon crystals should be impeded more effectively than that of the aluminum crystals by the presence of a given amount of sodium. It is a general rule that the metallic elements crystallize more vigorously than the non-metallic elements and metalloids like silicon. It even seems that the amount of sodium which produces the maximum refinement of silicon is just about the amount to produce germinative conditions with respect to aluminum

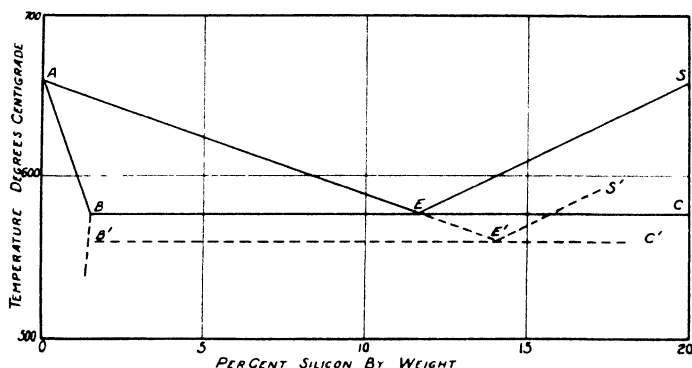


FIG. 5.—CONSTITUTION DIAGRAM OF ALUMINUM-SILICON ALLOYS.

and correspondingly large dendrite size. There is also a possibility that there is a selective attraction between sodium and silicon which is greater than that between aluminum and sodium. This is consistent with the fact that sodium is only slightly soluble in liquid aluminum.

It is evident from the photomicrographs in Figs. 1 and 3 that there is an apparent shifting of the eutectic composition. This will be readily understood on referring to the diagram in Fig. 5. The dotted lines represent in a qualitative way conditions attained when undercooling takes place as in the presence of sodium. The line $E'S'$ represents the temperatures of separation of primary silicon under conditions resulting in maximum suppression of crystallization. It will be noted that no dotted line has been drawn under AE to represent undercooling with respect to aluminum. Theoretically it is probable that some undercooling takes place, but it seems to be so slight as compared to undercooling with respect to silicon that it is justifiable to omit this factor from considera-

⁶ Zay Jeffries and R. S. Archer: Grain Growth and Recrystallization in Metals. *Chem. & Met. Engng.* (1922) **26**, 343, 402, 449.

tion. The line AE has been prolonged as a straight line until it intersects the line $E'S'$. The point E' therefore represents the composition of the alloy which under maximum conditions of suppression will solidify at the lowest temperature and without the appearance of either primary aluminum or primary silicon. This may well be called the modified eutectic alloy. It is not to be understood that this conception applies to equilibrium conditions. Under equilibrium conditions there can be only one eutectic alloy and one eutectic temperature; namely, the normal eutectic containing about 11 per cent. silicon and freezing at 577° C.

OCCURRENCE OF IRON IN ALUMINUM-SILICON ALLOYS

Iron is always present in aluminum-silicon alloys as an impurity. It is practically insoluble in the solid state, and the presence of even a few hundredths per cent. causes the appearance of a distinct "iron constituent." The manner of occurrence of this constituent is illustrated in Figs. 1, 2 and 4, and will be further illustrated in subsequent photomicrographs. In unetched sections the iron constituent appears in halftone; *i. e.*, darker than the aluminum and lighter than the silicon. In the alloys under consideration the iron constituent is generally in the form of plates, needles or perhaps flakes of irregular shape. These particles are refined somewhat by the modifying process.

The composition of the iron constituent in aluminum-silicon alloys is not definitely known. It is not the $FeAl_3$ of the binary aluminum-iron system, but is probably a ternary constituent containing iron, silicon and aluminum.

THE MODIFYING PROCESS

With the introduction of his process, Pacz disclosed that if an aluminum-silicon alloy is allowed to stand in the molten condition for too long a time after the flux treatment, the modification effect is gradually lost, and that if a properly modified cast alloy is remelted and again cast without any further treatment, it reverts almost entirely to the normal condition. The discovery of the metallic-sodium method of modifying indicated that this reversion to the normal condition on standing in the molten state or on remelting is due to the loss of sodium. In fact there are visible signs of such loss. Subsequent experience has demonstrated as a practical certainty that the actual loss of sodium is the dominant factor in this reversion, although it is conceivable that there is some effect due to a change in the distribution of the sodium.

The reversion from the modified to the normal condition is gradual rather than abrupt. By pouring at various intervals of time after the proper execution of the fluxing treatment, it is possible to obtain castings varying continuously in structure and properties from the completely

modified to the normal. Furthermore, it was early recognized that when insufficient quantities of flux are used, the castings obtained are only partly modified. The usual recommendations called for an amount of flux equal to about 3 per cent. by weight of the metal treated. This flux contains two parts sodium fluoride to one part sodium chloride and is applied at about 927° C. (1700° F.).

One of the first important results of the work leading to this paper was the establishment of the fact that poor modification results from the use of too much sodium as well as from too little sodium, whether the sodium be derived from the salt flux or added directly as metallic sodium. In fact, it is possible, by the use of too much sodium, to make the properties of the "modified" alloys inferior to those of the normal alloys.

For a long time after the discovery that the aluminum-silicon alloys can be modified by the addition of metallic sodium, it appeared somewhat doubtful that this method would give as good physical properties as the flux method. After trying both methods, several laboratories and foundries in various parts of the world concluded that the flux method gave better results, although the economy of the metallic sodium method was universally recognized. For this reason the flux method has been used by many in preference to the metallic-sodium method, in spite of the much greater economy of the latter.

The same conclusion seemed to be indicated by the first work in the laboratories of the Aluminum Co. of America, but it was soon shown that the best results obtained by the flux method are no better than the best results obtained by the metallic-sodium method. It still seemed for some time that the flux method gave good results with greater uniformity and certainty than the metallic-sodium method, but after considerable experimentation, it was found possible to control the modifying process based on metallic sodium in such a way that the uniformity of results obtained both in laboratory and foundry fully equalled that obtained by the use of the flux. It now appears that the metallic-sodium method will be almost exclusively used in commercial practice. The following paragraphs detail the more important considerations involved in the successful operation of the process.

Quantity of Sodium Required

Probably the most important requirement for successful modification is that the molten alloy contain the proper amount of sodium well distributed at the time of casting. The amount of sodium required to produce the best results appears to be definite for a given alloy and for given casting conditions. The sodium requirement varies over a wide range with the composition of the alloy, particularly the silicon content, as will be shown subsequently. For a given alloy, the sodium requirement also varies with the rate of solidification, the general rule being that less

sodium is required as the rate of solidification increases. The present discussion refers to test bars $\frac{1}{2}$ in. in diameter poured from about 705° C. (1300° F.) into green-sand molds. The results may be considered applicable to the general run of sand castings having sections up to about one inch thick. It is probable that somewhat larger quantities of sodium should be used where heavier sections predominate, but this factor has not yet been systematically investigated.

There has not been developed any simple and accurate method of determining the amount of sodium actually present in a modified casting. Such information would be interesting, but would perhaps not be of much practical use unless there were also some means of determining the sodium content of the molten alloy before casting. From the practical standpoint, the thing of interest is the quantity of sodium which must be added to the molten metal. If the conditions of the modifying process are kept constant, then the quantities of sodium present in the modified castings should be definitely related to the quantities added, although not necessarily directly proportional thereto. The amount of sodium in the metal at the time of casting will be determined by (1) the quantity added; (2) the efficiency of the addition; and (3) the loss before pouring into castings.

Method of Adding Sodium

When it is considered that sodium and aluminum are almost entirely immiscible in the liquid state, that sodium is much lighter than aluminum, that it is highly inflammable and that its boiling point is in the range of ordinary melting temperatures for aluminum, it will be realized that it is no simple matter to make a quantitative addition of sodium to a molten aluminum-silicon alloy. It is beyond the scope of this paper to discuss the various methods that have been proposed or tried, and the discussion will be confined to one method which is simple and economical and has been found suitable for both laboratory and production work.

The alloy is melted in a suitable crucible, pot or furnace, care being taken to avoid contamination with iron. A crucible or ladle from which the castings are to be poured is preheated to a red heat, say about 538–705° C. (1000–1300° F.) The required quantity of sodium is accurately weighed and kept covered with kerosene until used. When the metal has reached a suitable temperature, which will usually be about 774° C. (1425° F.), the sodium is placed in the bottom of the preheated pouring crucible or ladle. The molten metal is then immediately poured into this crucible in such a way as to stir the sodium into the aluminum as much as possible. This is ordinarily the only stirring employed.

The temperature of the metal at the time of pouring on to the sodium can be varied somewhat to suit the requirements of the foundry, but any such variation will affect the quantity of sodium to be used. The loss

of sodium in this operation increases with the temperature of the metal, especially when this temperature exceeds about 802°C . (1475°F .) The metal temperature should be controlled within 14°C . (25°F .) for consistent results.

The temperature of the preheated pouring crucible need not be controlled so closely, the temperature range given above being satisfactory. The object of preheating this crucible is to delay the subsequent cooling of the metal.

On throwing the sodium into the hot crucible, yellow flames will be observed. These are not ordinarily due to the combustion of sodium, but to the burning of the kerosene, which seems to protect the sodium for perhaps as much as a minute. The efficiency of sodium introduction by this method appears to be quite high, especially when the metal temperature is low.



FIG. 6.—METHOD OF POURING TEST BARS USED IN THIS WORK.

LOSS OF SODIUM ON STANDING

It has been found advantageous to allow the molten alloy to stand quietly for some time after the addition of sodium. The function of this holding period is partly to allow the escape of the air and dross stirred into the metal with the sodium. The benefits actually obtained, however, seem too great to attribute entirely to this cleansing action. It is quite possible that during this period there is a diffusion of sodium through the alloy, and an escape of the larger particles of undissolved sodium by rising to the surface. Good modification has been obtained by adding a small amount of sodium and casting immediately afterwards. It seems, however, that maximum properties are obtained more consistently by adding an excess of sodium and allowing the metal to stand quietly for a certain period. It is recommended that this period be not less than five minutes, and better ten to twenty minutes.

There is a continuous loss of sodium during the holding period, and the rate of this loss will obviously vary with conditions, such as the tem-

perature of the metal and the size and shape of the container. It has been found, as would be expected, that the loss increases with the metal temperature, although no quantitative relations have been developed. The problem is one whose solution is easier by empirical than by analytical methods. A method for reaching a practical solution will be discussed toward the close of this paper.

EXPERIMENTAL METHODS

Raw Materials.—The alloys studied in this investigation were made from commercial grades of ingot and aluminum-silicon rich alloy. These materials were selected so that alloys could be prepared having iron contents around 0.35 per cent., which is about as low as is encountered in present commercial practice. Iron was added in the form of Armeo iron wire (about 99.85 per cent. iron).

The aluminum ingot used was all from the same lot, but was remelted in two heats of 200 lb. each and cast in the form of smaller ingots, for greater convenience in handling and for greater uniformity of composition. The analyses of these two heats are given in Table 1, under samples 3807 and 4047. Four lots of silicon-rich alloy were used, the analyses of which are given in Table 1. Two of these, samples 3950 and 4024 were remelted while the others were not. The remelting was carried out in an oil-fired iron pot furnace, the pot being coated with a wash to prevent absorption of iron.

TABLE 1.—*Chemical Analyses of Raw Materials*

Sample Number	Material	Chemical Composition			
		Iron, Per Cent	Silicon, Per Cent	Copper, Per Cent	Manganese, Per Cent
3807	Aluminum ingot	0 41	0 29	0 01	Nil
3850	Silicon-rich alloy	0 36	17 08	0 04	0 03
3864	Silicon-rich alloy	0 33	16 48	0 03	0 02
3950	Silicon-rich alloy	0 30	16 00	0 02	0 01
4024	Silicon-rich alloy	0 32	15 95	Trace	
4047	Aluminum ingot	0 46	0 36	Trace	

Melting of Alloys

In most cases the alloys to be investigated were made up in heats of 20 to 25 lb., melted in a No. 25 plumbago crucible in a Stewart oil-fired brass melting furnace. When melted, the metal was thoroughly stirred with a carbon rod. Additions of iron were made after the metal had reached a temperature of about 815° C. (1500° F.). Iron dissolves readily if care is taken to clean the wire and to prevent it from becoming coated with aluminum dross when it is introduced into the melt. Undis-

solved iron can be easily detected with a carbon rod if the wire is twisted into a coil before being added to the melt.

The maximum temperatures in melting were about 815° C. (1500° F.) except that when iron was added the temperature was raised somewhat to hasten solution of the iron.

Modifying

The melt was removed from the furnace at about 815° C. (1500° F.) and set on the floor to cool. Meanwhile a pouring crucible, of the same kind and size as the melting crucible, was placed in the furnace. It was found possible to preheat this crucible to the desired temperature, about 649° C. (1200° F.), by the time the metal had cooled to the modifying temperature, 774° C. (1425° F.). The empty crucible was then removed from the furnace, the previously weighed sodium dropped into it, and the metal skimmed and poured over the sodium. At this point a timer was

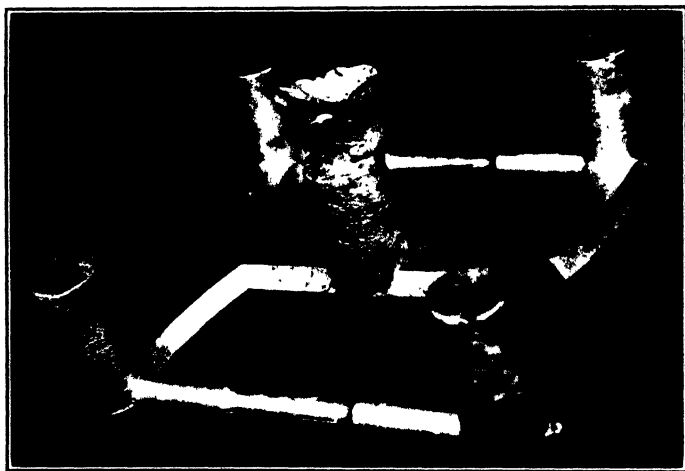


FIG. 7.—COMMON METHOD OF CASTING TEST BARS IN ALUMINUM FOUNDRIES.

started. The metal was then replaced in the hot furnace to prevent too rapid cooling. No stirring or skimming was done after the introduction of the sodium except that the dross was pushed back from the lip of the crucible on pouring.

One mold of test bars was poured five minutes after the introduction of the sodium, and additional molds were poured at three-minute intervals thereafter until eight molds had been poured, the metal being held in the furnace between pouring operations. The metal was usually at a temperature between 734° and 752° C. (1350° to 1390° F.) when the first mold was poured, and was between 675° and 734° C. (1250°–1350° F.) for the rest of the molds.

It was pointed out above that it is desirable to add a slight excess of sodium and allow the metal to stand several minutes before pouring castings, the excess of sodium being eliminated during this holding period. In these experiments it was attempted to add such amounts of sodium that, under the conditions employed, the metal would attain its maximum degree of modification when poured about seventeen minutes after the addition of sodium. If all molds were poured at this time, however, there would be no way of telling whether the optimum sodium content had been attained, except by many experiments. By pouring molds at intervals as described above, test bars were obtained in which the sodium content decreased gradually and by small decrements as the time after the addition of sodium increased. Typical results obtained by this method will be presented and discussed subsequently.

Preparation of Normal Alloys

Although the primary object of this work was the investigation of the modified alloys, it was thought of interest to examine some of the alloys in the normal condition. For this purpose test bars were cast before the addition of sodium. The raw materials, however, often contain some sodium, and such traces of sodium may cause partial modification. It is possible, therefore, that slightly lower physical properties would be obtained from alloys strictly free from sodium.

Test-bar Mold

Fig. 6 shows the method of molding test bars that was employed in most of this work. A few castings were made as shown in Fig. 7, which illustrates the usual method of pouring test bars in the foundries of the Aluminum Co. of America. In the case of the alloys under investigation, these two molds gave substantially the same results. The mold shown in Fig. 6, therefore, was generally used, as it required only about half as much metal as that of Fig. 7.

The test bars were cast to size, the test section having a diameter of $1\frac{1}{2}$ in. with a length of $21\frac{1}{4}$ in. between fillets. Elongation was measured on a gage length of 2 in. The ends of the test bar were $3\frac{1}{4}$ in. in diameter.

Testing

All test bars were tested without machining in a 50,000-lb. Olsen testing machine using wedge grips. The ductility of these alloys is such that any errors introduced by slight imperfection of alignment are well within the variations between individual test bars. As a rule only tensile strength and elongation were determined. No room-temperature aging effect has been observed in these alloys, but it may be mentioned that tests were usually made within 24 hr. after casting.

Microscopic Examination

Samples for microscopic examination were taken from the test sections of broken test bars, the surface prepared for examination being generally taken perpendicular to the axis of the bar. There are sometimes objections to the use of specimens which have been strained, but in this work the fact that the metal had been tested in tension did not seem to interfere with the objects of the microscopic examinations, and it was obviously a considerable advantage to correlate the structures definitely with tensile properties previously determined for identically the same sections.

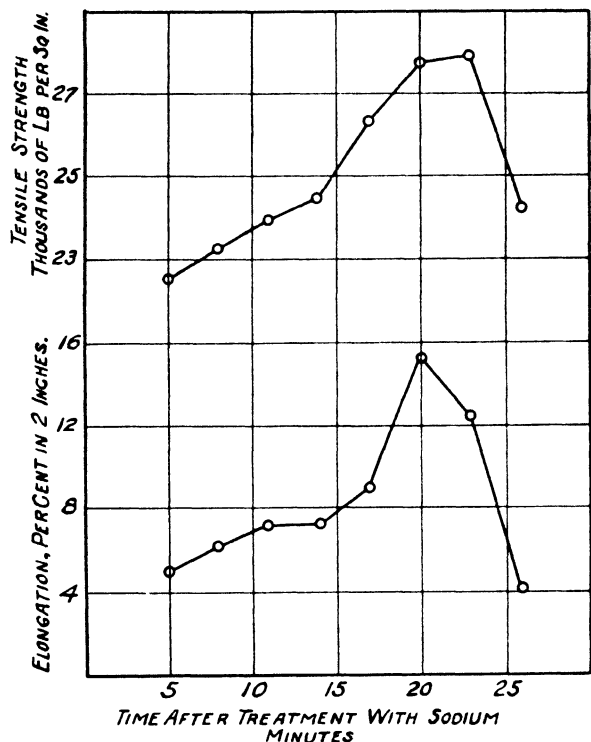


FIG. 8.—EFFECT OF TIME OF HOLDING AFTER ADDITION OF SODIUM ON PHYSICAL PROPERTIES OF MODIFIED ALUMINUM-SILICON ALLOY. SAMPLE 3866.

Chemical Analysis

Drillings for analysis were taken from test bars or from the runners connecting the test bars. In the case of aluminum ingot and remelted rich alloys, special samples were cast in the form of thin plates in an iron mold. Precautions must be taken against segregation which is especially apt to occur in alloys containing more than about 14 per cent. silicon.

The aluminum ingot and rich alloys were analyzed for silicon, iron, copper, and manganese. The elements determined in the final alloys were silicon or iron or both.

RESULTS

The effect of the time element in the modifying process is illustrated by the data in Table 2 and in Fig. 8, from a typical experiment in which test bars were poured at various intervals after the addition of sodium, as described above. Tensile strength and elongation increase steadily to maximum values with the time after the addition of sodium, and then fall off rapidly toward values characteristic of the unmodified alloy. This means that during the first few minutes the metal contains too much sodium, and constantly becomes better primarily because of loss of sodium. At a certain time, in this case about twenty minutes after the addition of sodium, the sodium content is just right for the production of a well modified structure on casting. On further holding, the

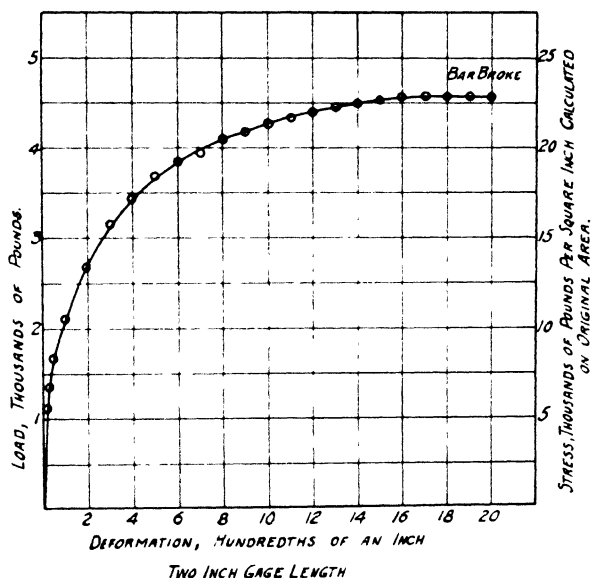


FIG. 9.- LOAD DEFORMATION CURVE OF MODIFIED ALLOY CONTAINING 10 PER CENT. SILICON. SAMPLE 4045.

molten metal continues to lose sodium, the properties of the test bars falling off as the sodium content becomes insufficient to produce complete modification.

Table 2 and Fig. 8 show that the maximum tensile strength does not occur at exactly the same time as the maximum elongation. This has frequently been noted and seems to be characteristic of the alloys. The relation is always about as shown; that is, the elongation reaches a maximum slightly before the tensile strength and then decreases rather more abruptly than the strength. The sharp cusp of the elongation curve is due, of course, to the fact that the molds were poured 3 min. apart. The true form of the curve at the maximum is more flat, and the

form actually obtained as the result of experiment depends on when the test bars are poured with relation to the time of occurrence of the true maximum.

TABLE 2.—*Effect of Time after Treatment with Sodium*

Sample No. 3866

Mold No.	Time after Sodium Treatment, Minutes	Tensile Strength, Lb. per Sq. In.	Elongation Per Cent. in 2 In.	Remarks
1	5	22,200	4.0	Dross
1	5	22,950	6.0	
Average.		22,575	5.0	
2	8	22,375	5.0	Sand hole
2	8	24,175	7.5	
Average		23,275	6.25	
3	11	23,675	7.0	
3	11	24,290	7.5	
Average		23,987	7.25	
4	14	24,400	7.0	Dross
4	14	24,600	7.5	
Average		24,500	7.25	
5	17	26,625	10.0	
5	17	26,000	8.0	
Average		26,313	9.0	
6	20	27,725	14.5	
6	20	27,750	16.0	
Average		27,735	15.25	
7	23	(25,825)	(7.0)	Dross
7	23	27,800	12.5	
Average		27,800	12.5	
8	26	24,050	4.5	
8	26	24,450	4.0	
Average		24,250	4.25	

Elongation appears to be more sensitive than tensile strength to the degree of modification. Some light is thrown on the reason for this by the load-deformation curve, Fig. 9, of a test bar of a 10 per cent. silicon alloy, sample 4045. It is here shown that much of the elongation occurs as the result of relatively small changes in load. The elongation actually increased from 8 per cent. to 10 per cent. at practically constant load. The effect of this characteristic of the load-deformation curve will readily be understood. The presence of a minute source of weakness,

either an actual flaw in the bar or a region in which the modification is poor, will cause only a slight decrease in tensile strength but a relatively much larger decrease in elongation.

The increase in elongation is perhaps the most valuable effect of modification, not only because the increase in this property is relatively much greater than in any other property, but also because of the demand for light aluminum alloys having good ductility combined with fair strength and good casting qualities.

In view of the importance of this property, and its sensitivity to the condition of the metal, elongation was selected as a criterion of proper

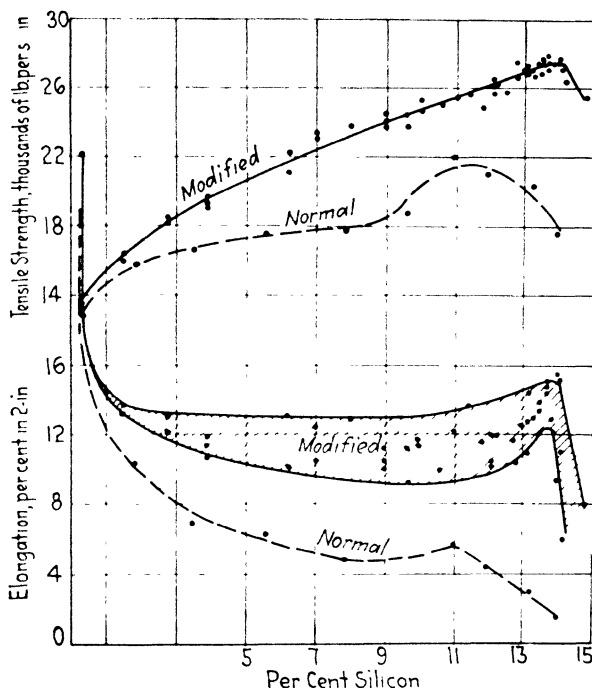


FIG. 10. --PHYSICAL PROPERTIES OF NORMAL AND MODIFIED ALUMINUM-SILICON ALLOYS CONTAINING ABOUT 0.35 PER CENT. IRON.

modification. The values of strength and elongation taken as typical of any given alloy composition were the average properties of the sound bars from the mold or molds showing the maximum elongation of the series. The fractures of the bars were examined for the presence of dross, holes, etc., and such defects were recorded with the results of the tests. If the defect obviously reduced the properties of the bar to a marked extent, the results of the test were discarded. In other cases the effects of the flaws were so slight that the results of the tests could be included for the purpose of arriving at more representative averages. Table 2 illustrates the manner of selecting typical values.

Although it is felt that the attempt to control the modifying process has been fairly successful, it is not meant to give the impression that the control is perfect or that the best possible results are always obtained, even in the laboratory. In some experiments it was obvious that none of the test bars was properly modified. This could be judged from the microstructure, the fracture, or the maximum properties as compared with those of other heats of similar composition. In such cases the experiments were repeated with any changes thought to be indicated by the conditions. If the repetition of the experiment gave distinctly better values, the results of the first experiment were discarded, while if the remelt gave about the same values as the original, the

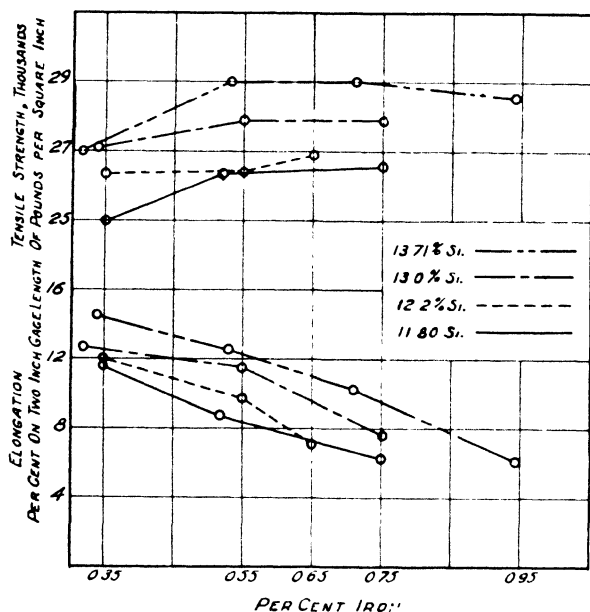


FIG. 11.—EFFECT OF IRON CONTENT ON PHYSICAL PROPERTIES OF MODIFIED ALLOYS CONTAINING 11 TO 14 PER CENT. SILICON.

results of both experiments were recorded. In this way it was attempted to get values as representative as possible of each alloy in its best state of modification. It is too much to hope that this attempt was in all cases completely successful. Attention was concentrated largely on the modified alloys containing from 12 to 14 per cent. silicon, and the results should be most reliable for alloys in this range of composition.

Table 3 gives the composition by chemical analysis of the alloys studied. In some cases alloys were remelted and given different sample numbers. Therefore, there will be found in the subsequent tables certain sample numbers not found as such in Table 3. The compositions given

TABLE 3.—*Chemical Analyses of Alloys Studied*

Sample Number	Silicon, Per Cent	Iron, Per Cent	Copper, Per Cent	Sample Number	Silicon, Per Cent	Iron, Per Cent	Copper, Per Cent.
3851	14.13			3948	13.82	0.92	
3853	13.86			3949	12.50	0.65	
3855	13.70	0.33		3951	13.71	0.34	0.02
3857	14.06	0.37	0.02	3952	13.0	0.32	0.02
3859	14.08			3953	13.73	0.53	
3862	13.50	0.37	0.015	3956		0.71	
3865	14.20			3959		0.55	
3866	13.73			3963	11.38	0.35	
3869	13.13			3974		0.75	
3870	12.80			3979		0.77	
3871	12.18	0.36	0.01	3980	13.80	0.89	
3872	12.32			4017	13.21	0.32	0.04
3881	11.80			4023	14.80	0.35	0.01
3886	13.11			4026	13.55		
3893	10.62	0.34	0.01	4027	4.83	0.39	Trace
3918	13.86	0.55		4028	7.04	0.35	Trace
3926	13.41	0.77	0.02	4032	9.03	0.34	
3928	11.67	0.52		4035	11.02	0.34	
3929	12.75	0.36	0.03	4036	2.75	0.44	Trace
3932	12.90	0.58		4041	7.95	0.40	
3933	11.86	0.75		4043	6.18	0.40	
3937	12.82	0.80		4044	9.62	0.39	
3939	13.28	0.36	0.01	4046	12.19		
3940		0.56		4048	1.51	0.46	
3941	13.21	0.75		4049	0.35	0.47	Trace
3946	13.26	0.95		4054	3.90		
3947	13.53	1.01		4062	10.11	0.38	0.01
				4064	3.46		
				4065	7.79		
				4066	9.61	0.40	
				4068	1.84	0.42	0.01
				4069	5.55	0.43	
				4078	14.02		
				4080	11.87		

in these subsequent tables for such samples are based on analyses of the heats from which these samples were derived.

Table 4 gives the physical properties of some of the alloys in the normal condition. These alloys constitute a series in which the silicon content varies from that of the original ingot (0.29 per cent.) up to about 14 per cent., the iron content being held practically constant at an average value of about 0.35 per cent.

In Table 5 are given the physical properties of a much more complete series of alloys in the modified condition, covering about the same range of silicon content and with the iron content again constant at an average

value of about 0.35 per cent. There are also given the quantities of sodium that were added, and the periods of time between the addition of the sodium and the attainment of the highest elongation. In this connection it is to be remembered that, after the first five minutes, the molds were poured three minutes apart. The values given in the time column do not, therefore, always correspond exactly to the true maxima.

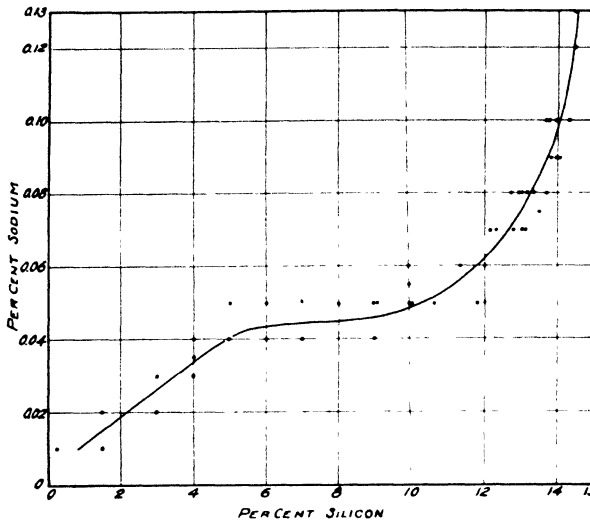


FIG. 12.—EFFECT OF SILICON CONTENT OF ALLOYS ON QUANTITY OF SODIUM REQUIRED FOR MODIFICATION.

TABLE 4.—Physical Properties of Normal Alloys

Sample Number	Silicon, Per Cent	Iron, Per Cent	Tensile Strength, Lb. per Sq. In.	Elongation Per Cent in 2 In.
4049	0.29	0.41	12,790	25.0
4068	1.84	0.42	15,795	10.4
4064	3.46		16,715	7.0
4069	5.55	0.43	17,382	6.2
4065	7.79		17,800	4.9
4066	9.61	0.40	18,882	4.9
4035	11.02	0.34	22,175	5.7
4080	11.87		21,150	4.4
4017	13.21	0.32	20,225	3.0
4078	14.02		17,794	1.6

Table 6 gives similar data for several series of modified alloys in each of which the silicon content was held constant while the iron content was increased by the addition of Armco iron wire.

TABLE 5.—*Physical Properties of Modified Alloys*
Effect of Silicon

Sample Number	Silicon, Per Cent	Iron, Per Cent.	Tensile Strength, Lb. per Sq. In.	Elongation Per Cent. in 2 In.	Per Cent Sodium Added	Time to Best Properties, Minutes
4049	0.29	0.41	13,500	28.2	0.01	20
4048	1.51	0.46	16,270	13.7	0.02	26
4051	1.51	0.46	15,925	13.2	0.01	23
4036	2.75	0.44	18,375	12.2	0.03	17
4056	2.75	0.44	18,325	13.0	0.02	20
4054	3.90	0.40	19,170	11.5	0.03	20
4060	3.90	0.35	19,300	11.5	0.035	14
4063	3.90	0.35	19,750	10.7	0.04	17
4027	4.83	0.39	20,725	13.0	0.05	20
4042	6.18	0.40	21,170	10.2	0.03	11
4043	6.18	0.40	22,300	13.0	0.04	17
4028	7.04	0.35	23,050	10.5	0.05	23
4052	7.0	0.35	23,150	12.5	0.04	17
4041	7.95	0.35	23,825	13.0	0.05	20
4032	9.03	0.34	24,300	11.2	0.05	20
4039	9.03	0.34	23,670	10.2	0.04	17
4072	9.0	0.35	24,125	10.2	0.05	20
4044	9.62	0.39	24,450	11.2	0.05	17
4045	9.62	0.39	23,850	9.5	0.05	17
4055	10.11	0.35	24,725	11.5	0.055	14
4062	10.11	0.35	25,300	11.7	0.06	20
3893	10.62	0.34	25,100	10.0	0.05	17
4035	11.02	0.34	25,500	12.2	0.05	8
3963	11.38	0.35	25,770	13.7	0.06	23
3881	11.80	0.35	24,915	11.5	0.05	17
4046	12.19	0.35	26,250	10.5	0.05	14
4053	12.19	0.35	25,710	10.5	0.06	17
3871	12.18	0.36	26,300	12.0	0.07	20
3872	12.32	0.35	26,300	12.0	0.07	17
3929	12.75	0.36	26,590	11.7	0.08	26
3870	12.80	0.35	27,600	10.5	0.07	23
3952	13.00	0.32	27,000	12.7	0.08	20
3886	13.11	0.35	26,925	11.0	0.07	17
3869	13.13	0.35	27,155	12.0	0.07	17
4017	13.21	0.32	26,950	14.5	0.08	20
3939	13.28	0.36	26,730	13.0	0.08	23
3892	13.40	0.35	27,425	12.0	0.08	17
3862	13.50	0.37	26,925	14.7	0.075	17
4026	13.55	0.35	27,775	13.5	0.10	11
4077	13.55	0.35	27,562	14.0	0.10	17
3855	13.70	0.33	28,000	14.7	0.08	20
3951	13.71	0.34	27,110	14.5	0.10	23
3866	13.73	0.35	27,735	15.0	0.10	20
3853	13.86	0.35	27,470	13.0	0.09	11
3857	14.06	0.37	27,790	15.5	0.09	17
3859	14.08	0.35	27,600	9.5	0.10	20
3851	14.13	0.35	27,360	11.0	0.10	20
3865	14.20	0.35	26,520	6.0	0.10	20
4023	14.80	0.35	25,450	8.0	0.13	20

In Fig. 10 the physical properties of the normal and modified alloys containing about 0.35 per cent. iron are plotted against silicon content. In the case of the modified alloys, elongation is represented by an area rather than by a line.

The effect of iron on the modified alloys is illustrated in Fig. 11. Strength and elongation are plotted against iron content for four series of alloys of different silicon content.

Fig. 12 shows how the amount of sodium required for modification varies with the silicon content of the alloy to be modified. The percentages of sodium plotted are those added to the melt. The amounts actually present at the time of casting are less.

TABLE 6.—*Physical Properties of Modified Alloys*
Effect of Iron

Sample Number	Silicon, Per Cent.	Iron, Per Cent	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent in 2 In.	Per Cent Sodium Added	Time to Best Properties, Minutes
3963	11.38	0.35	25,770	13.7	0.06	23
3977	11.38	0.55	26,390	10.0	0.06	20
3979	11.38	0.77	25,110	5.0	0.07	23
3881	11.80	0.35	24,915	11.5	0.05	17
3928	11.80	0.52	26,360	8.7	0.07	14
3933	11.80	0.75	26,550	6.2	0.07	20
3872	12.28	0.35	26,300	12.0	0.06	17
3921	12.28	0.55	26,390	9.7	0.08	11
3949	12.28	0.65	26,870	7.0	0.08	17
3929	12.79	0.36	26,590	11.7	0.08	26
3932	12.79	0.58	27,920	9.2	0.08	20
3937	12.79	0.80	28,570	7.5	0.10	20
4104	12.79	1.0	23,825	2.5	0.11	17
3952	13.0	0.32	27,000	12.7	0.08	20
3959	13.0	0.55	27,870	11.5	0.08	20
3974	13.0	0.75	27,880	7.5	0.08	20
3939	13.28	0.36	26,730	13.0	0.08	23
3940	13.28	0.56	27,820	10.0	0.08	23
3941	13.28	0.75	28,445	10.5	0.08	23
3946	13.28	0.95	22,300	2.7	0.09	8
3923	13.41	0.35	27,400	12.2	0.08	20
3924	13.41	0.55	28,340	10.5	0.08	17
3926	13.41	0.77	29,050	9.5	0.06	11
3947	13.41	1.01	24,400	2.0	0.08	17
3951	13.71	0.34	27,110	14.5	0.10	23
3953	13.71	0.53	28,920	12.5	0.10	26
3956	13.71	0.71	29,000	10.2	0.10	20
3980	13.71	0.89	28,500	6.0	0.10	20
3853	13.86	0.33	27,470	13.0	0.09	11
3918	13.86	0.55	28,650	11.5	0.11	11
3938	13.86	0.75	28,620	9.5	0.12	23
3948	13.86	0.92	28,260	5.5	0.12	17

MICROSTRUCTURE OF ALLOYS

The general structure of both the normal and modified alloys has been illustrated in Figs. 1, 2, 3 and 4. It seems of special interest to present a few additional photomicrographs illustrating some of the effects of silicon content and iron content on the microstructure of the modified alloys.

Figs. 13 to 19 show, at a magnification of 20 diameters, structures of a series of alloys containing about 0.35 per cent. iron and amounts of silicon increasing from 11.38 per cent. to 14.8 per cent. It will be noted that the areas occupied by the aluminum dendrites decrease as the

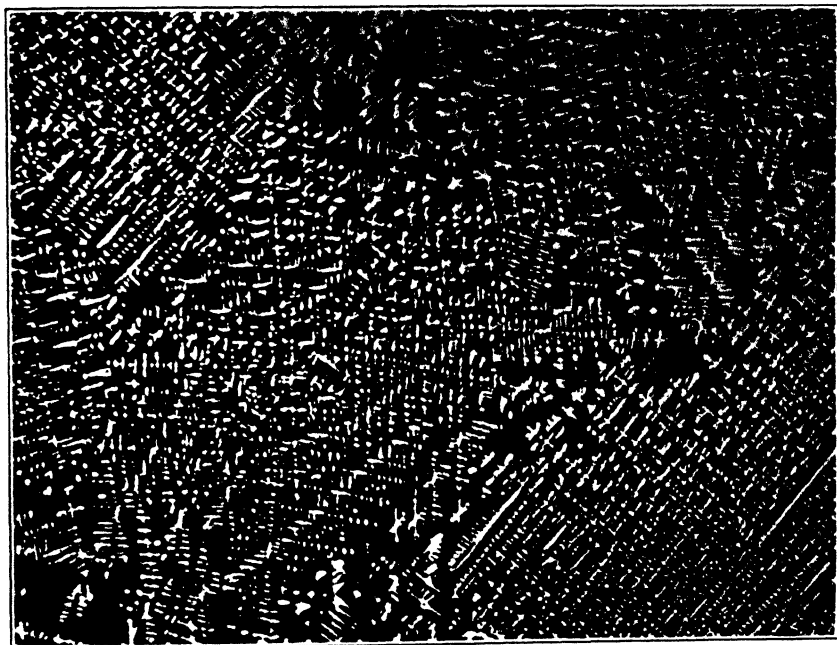


FIG. 13.—MODIFIED ALLOY CONTAINING 11.38 PER CENT. SILICON. SAMPLE 3963. TENSILE STRENGTH 25,770 LB. PER SQ. IN.; ELONGATION 13.7 PER CENT. ETCHED WITH 5 PER CENT. HF PLUS 10 PER CENT. HNO_3 . $\times 20$. WHITE ALUMINUM DENDRITES IN MATRIX OF MODIFIED EUTECTIC.

silicon content increases, disappearing at approximately 14 per cent. silicon. As the silicon content increases above 14 per cent. particles of excess silicon appear. This indicates that, with the best modification obtained in these experiments, the limiting composition of the modified aluminum-silicon eutectic is about 14.0 per cent. silicon.

Attention is called to Fig. 13, which shows the structure of a modified alloy having approximately the composition of the normal aluminum-silicon eutectic. The prevalence of the white aluminum dendrites is striking.

The alloy shown in Fig. 14 contains 12.75 per cent. silicon which is approximately the average silicon content of most of the modified sand castings which have been commercially produced. The appearance of aluminum dendrites is still striking, although there are areas of considerable size which are practically free from excess aluminum. It is obvious that in this specimen it would be easy to pick areas large enough for photomicrographs taken at higher magnifications, which would fail to show the relative amounts of modified eutectic and of excess constituent. It is for this reason that the present series was taken at a fairly low magnification.

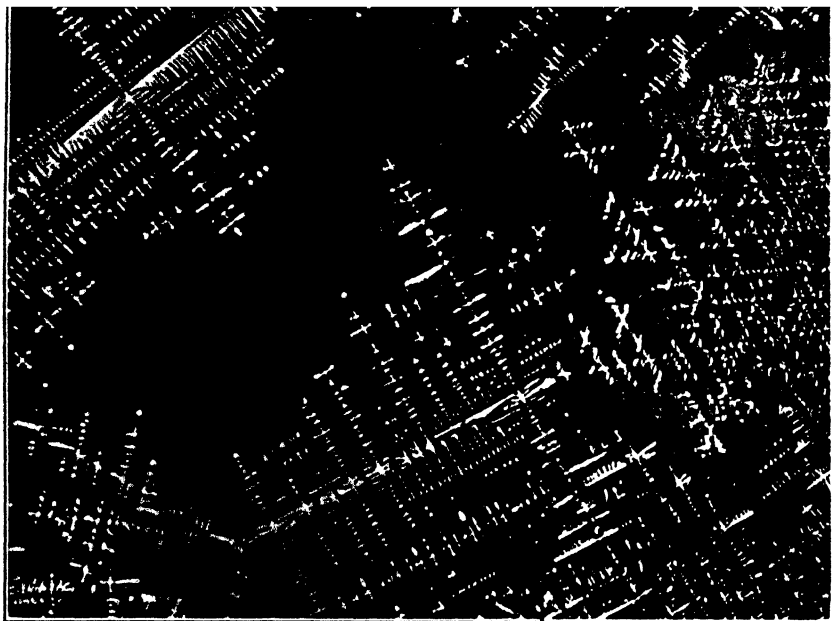


FIG. 14.—MODIFIED ALLOY CONTAINING 12.75 PER CENT. SILICON. SAMPLE 3929. TENSILE STRENGTH 26,590 LB. PER SQ. IN.; ELONGATION 11.7 PER CENT. ETCHED WITH 5 PER CENT. HF PLUS 10 PER CENT. HNO_3 . $\times 20$. NOTE DIFFERENT TINTS IN MATRIX INDICATING DIFFERENCES IN ORIENTATION OF EUTECTIC, CORRESPONDING WITH DIFFERENT ORIENTATIONS OF ALUMINUM DENDRITES.

Fig. 15 shows an alloy containing 13.73 per cent. silicon in which only a few aluminum dendrites were observed. Fig. 16 shows an alloy containing 14.06 per cent. silicon. The structure consists almost entirely of the modified aluminum-silicon eutectic.

In Fig. 17 is shown a specimen containing 14.08 per cent. silicon. This specimen shows a distinct excess of silicon occurring in the form of dark particles of nearly circular shape. The difference in silicon content as found by chemical analyses between this and the preceding specimen is too slight to account for the difference in structure or for the difference



FIG. 15.—MODIFIED ALLOY CONTAINING 13.73 PER CENT. SILICON. SAMPLE 3866. TENSILE STRENGTH 27,735 LB. PER SQ. IN.; ELONGATION 15.0 PER CENT. ETCHED WITH 5 PER CENT. HF PLUS 10 PER CENT. HNO_3 . $\times 20$.



FIG. 16.—MODIFIED ALLOY CONTAINING 14.0 PER CENT. SILICON. SAMPLE 3857. TENSILE STRENGTH 27,790 LB. PER SQ. IN.; ELONGATION 15.5 PER CENT. ETCHED

in elongation observed. These differences can be accounted for, however, on the assumption that sample 3859, shown in Fig. 17, is less perfectly modified than sample 3857, shown in Fig. 16. There is also a possibility of a small error in the sampling or in the chemical analysis.

The specimen shown in Fig. 18, which is reported to contain 14.20 per cent. silicon, shows a distinct excess of silicon in addition to the modified eutectic.

Fig. 19 shows a specimen containing 14.8 per cent. silicon in which the excess silicon is still more apparent. It has been observed that in alloys containing over 14 per cent. silicon the excess silicon tends to

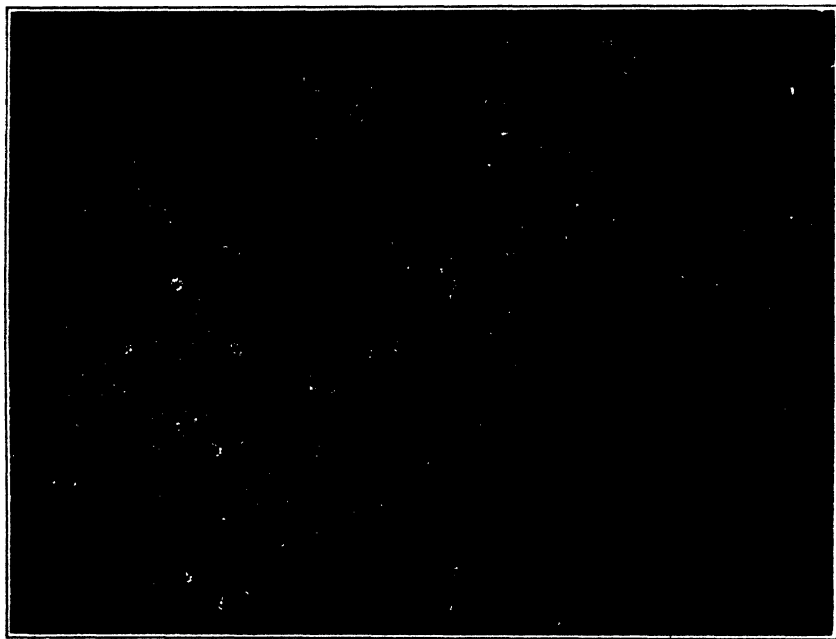


FIG. 17.—MODIFIED ALLOY CONTAINING 14.08 PER CENT. SILICON. TENSILE STRENGTH 27,600 LB. PER SQ. IN.; ELONGATION 9.5 PER CENT. ETCHED WITH 5 PER CENT. HF PLUS 10 PER CENT. HNO_3 . $\times 20$. THIS SPECIMEN SHOWS A FEW PARTICLES OF PRIMARY SILICON.

segregate in the upper part of the casting. There was a distinct segregation of silicon in this case in the upper half of the test bar. This is shown clearly in Fig. 20, which is a photograph of the entire cross-section of the test bar. The round black spots represent the excess silicon or in some cases cavities from which particles of excess silicon have been broken out in polishing. In making this test bar the two halves of the mold were slightly out of line, causing an offset at the parting line. The segregation of silicon is seen to be on the upper side of this parting line. When these alloys are poured into a green-sand mold, a thin shell of solid metal forms very quickly. If a mold is broken open shortly after

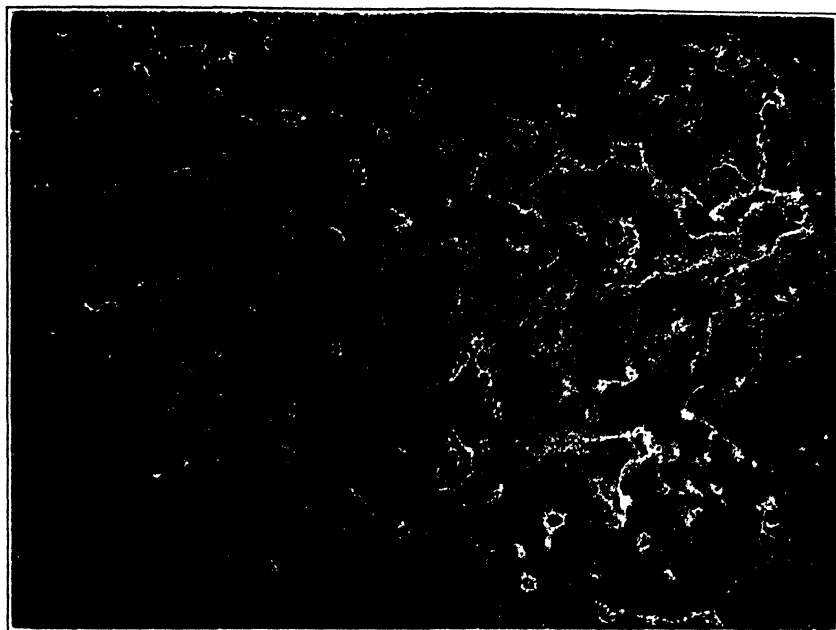


FIG. 18. - MODIFIED ALLOY CONTAINING 14.20 PER CENT. SILICON. SAMPLE 3865. TENSILE STRENGTH 26,520 LB. PER SQ. IN.; ELONGATION 6 PER CENT. ETCHED WITH 5 PER CENT HF PLUS 10 PER CENT. HNO_3 . $\times 20$. THIS SPECIMEN SHOWS NUMEROUS PARTICLES OF PRIMARY SILICON.

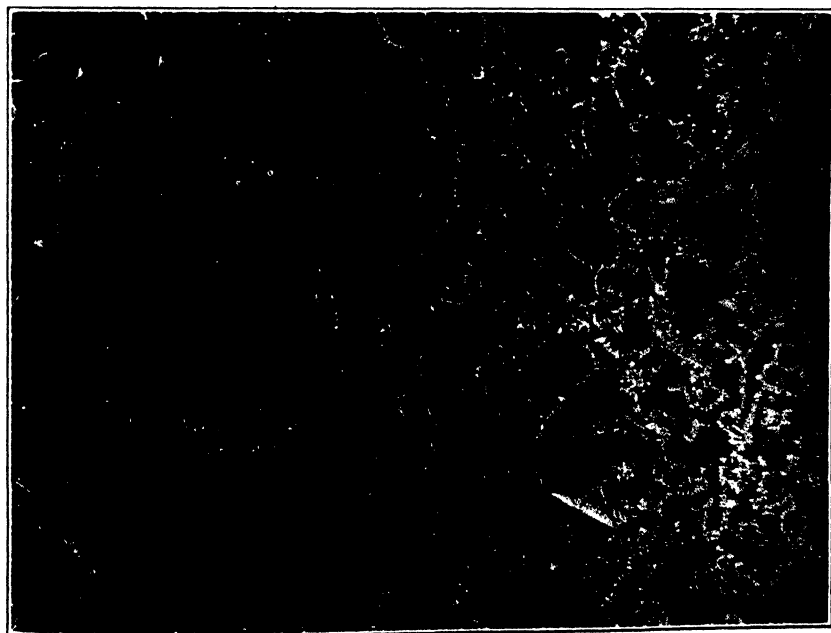


FIG. 19.—MODIFIED ALLOY CONTAINING 14.8 PER CENT. SILICON. SAMPLE 4023.

casting, the molten metal in the center can be poured out, leaving a slush casting of roughly tubular shape. It is probably during the relatively slow solidification of this molten interior that the particles of primary silicon separate and, being lighter than the molten alloy, rise to the upper portion of the casting. These particles do not quite reach the upper surface.

In Figs. 15 and 16 especially, appear some fine white lines or veins. These represent the same constituent as the white dendrites; that is,



FIG. 20.—CROSS-SECTION OF TEST BAR OF MODIFIED ALLOY CONTAINING 14.8 PER CENT. SILICON. SAMPLE 4023. ILLUSTRATING SEGREGATION OF PRIMARY SILICON IN UPPER HALF OF SECTION. UNETCHED. $\times 6$. THE BLACK DOTS REPRESENT EITHER PARTICLES OF PRIMARY SILICON OR CAVITIES FROM WHICH SUCH PARTICLES HAVE BEEN BROKEN IN POLISHING.

nearly pure aluminum containing a little silicon in solid solution. On closer examination they will also be found in many of the other photomicrographs.

On a cross-section of a test bar these veins are roughly parallel to the surface of the bar. Looking at the entire cross-section, the veins are seen to form a series of concentric rings centering about a point nearly at the geometric center of the section. When the amount of silicon exceeds

the composition of the modified eutectic, coarse particles of silicon begin to appear along the veins of aluminum.

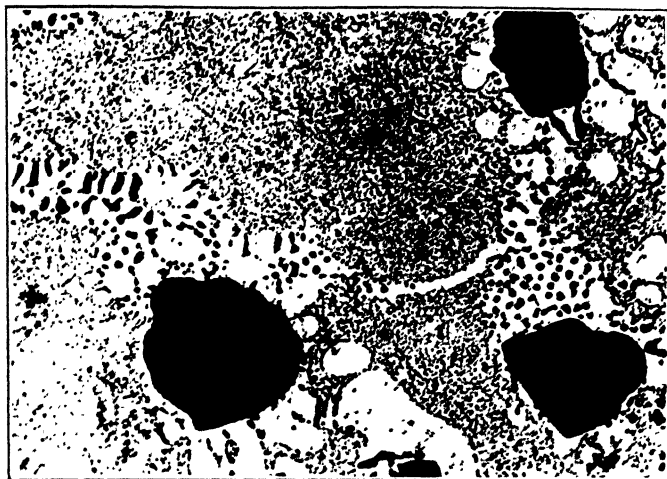


FIG. 21. SAME SPECIMEN AS IN FIG. 19 SHOWING SEGREGATED SILICON PARTICLES ILLUSTRATED IN FIG. 20. THE LARGE BLACK PARTICLES ARE PRIMARY SILICON. UNETCHED. $\times 100$.

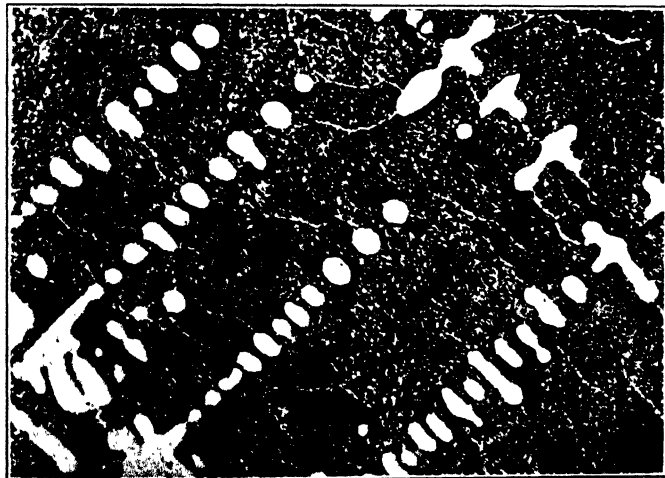


FIG. 22.—MODIFIED ALLOY CONTAINING 12.79 PER CENT. SILICON AND 0.36 PER CENT. IRON. SAMPLE 3929. TENSILE STRENGTH 26,590 LB. PER SQ. IN.; ELONGATION 11.7 PER CENT. DEEPLY ETCHED WITH 5 PER CENT. HF PLUS 10 PER CENT. HNO_3 . $\times 100$. THE IRON CONSTITUENT APPEARS IN THE FORM OF SHORT BLACK DASHES USUALLY CURVED.

Fig. 21 shows, at a magnification of 100 diameters, the segregated sample illustrated in Figs. 19 and 20. The large dark areas are the excess silicon particles. There can also be seen some of the silicon

particles of intermediate size, which were mentioned in the preceding paragraph as occurring along the white veins of aluminum. In many

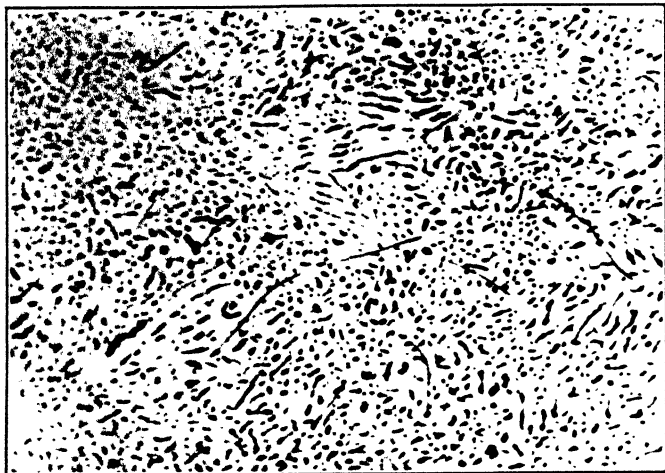


FIG. 23.—SAME SPECIMEN AS IN FIG. 22, ETCHED LIGHTLY WITH 0.5 PER CENT. HF. $\times 750$. SHOWS A PORTION OF THE EUTECTIC OF FIG. 22. THE IRON CONSTITUENT IS VISIBLE IN THE FORM OF THIN LINES USUALLY CURVED AND OF LIGHTER COLOR THAN THE BLACK PARTICLES OF SILICON.

cases these particles are strung out in a line along much more clearly marked aluminum veins.

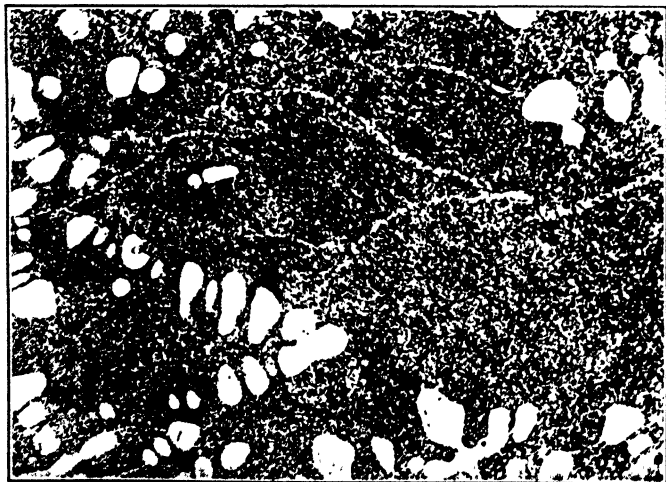


FIG. 24.—MODIFIED ALLOY CONTAINING 12.79 PER CENT. SILICON AND 0.58 PER CENT. IRON. SAMPLE 3932. TENSILE STRENGTH 27,920 LB. PER SQ. IN.; ELONGATION 9.2 PER CENT. DEEPLY ETCHED WITH 5 PER CENT. HF PLUS 10 PER CENT. HNO_3 . $\times 100$. THE IRON CONSTITUENT IS BLACK.

Figs. 22 to 29 show the change in structure of modified alloys containing 12.79 per cent. silicon as the iron content increases from 0.36 per

cent. to 1.0 per cent. The iron constituent increases in size as the iron content increases.



FIG. 25.—SAME SPECIMEN AS IN FIG. 24 BUT ETCHED VERY LIGHTLY WITH 0.5 PER CENT. HF. $\times 750$. THE IRON CONSTITUENT APPEARS IN HALFTONE.

Fig. 30 shows the structure of a modified alloy containing 2.75 per cent. silicon and 0.44 per cent. iron. The iron constituent is very much



FIG. 26.—MODIFIED ALLOY CONTAINING 12.79 PER CENT. SILICON AND 0.80 PER CENT. IRON. SAMPLE 3937. TENSILE STRENGTH 28,570 LB. PER SQ. IN.; ELONGATION 7.5 PER CENT. ETCHED DEEPLY WITH 5 PER CENT. HF PLUS 10 PER CENT. HNO_3 . $\times 100$. THE IRON CONSTITUENT IS BLACK. NOTE THAT SOME OF THE IRON CONSTITUENT OCCURS IN THE WHITE AREAS OF ALUMINUM.

coarser than in Fig. 22, in which the iron content of the alloy is nearly the same, but the silicon content very much higher. An explanation of

this is suggested by the fact that the iron constituent occurs almost entirely in the areas of aluminum-silicon eutectic. As the amount of silicon in the alloy decreases, the proportion of eutectic in the structure

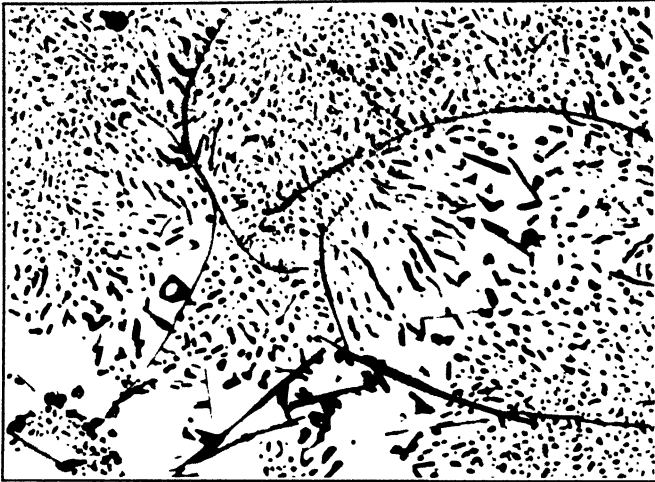


FIG. 27.—SAME SPECIMEN AS IN FIG. 26, BUT ETCHED LIGHTLY WITH 0.5 PER CENT. HF. $\times 750$. THE IRON CONSTITUENT APPEARS IN HALFTONE, THE SILICON BEING BLACK.

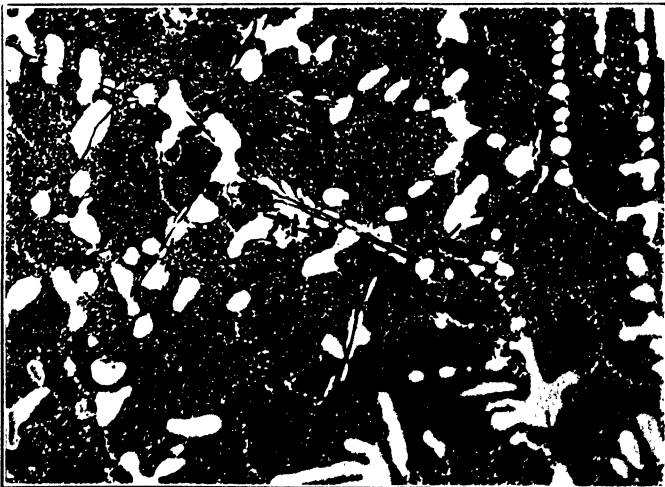


FIG. 28.—MODIFIED ALLOY CONTAINING 12.79 PER CENT. SILICON AND 1.0 PER CENT. IRON. SAMPLE 4104. TENSILE STRENGTH 23,825 LB. PER SQ. IN.; ELONGATION 2.5 PER CENT. DEEPLY ETCHED WITH 5 PER CENT. HF PLUS 10 PER CENT. HNO_3 . $\times 100$. THE IRON CONSTITUENT IS BLACK AND OCCURS PARTLY IN THE ALUMINUM.

decreases, and for a constant iron content in the alloy as a whole the percentage of iron in eutectic regions must increase.

DISCUSSION OF RESULTS

Referring to Fig. 10, it will be noted that the tensile strength of the normal alloys increases continuously from 12,800 lb. per sq. in. for sand-



FIG. 29.—SAML SPECIMEN AS IN FIG. 28, BUT ETCHED LIGHTLY WITH 0.5 PER CENT. HF. $\times 750$. THE IRON CONSTITUENT IS IN HALFTONE. SOME OF THE PARTICLES OF THE IRON CONSTITUENT APPEAR TO HAVE BEEN FRACTURED IN THE TENSILE TEST.

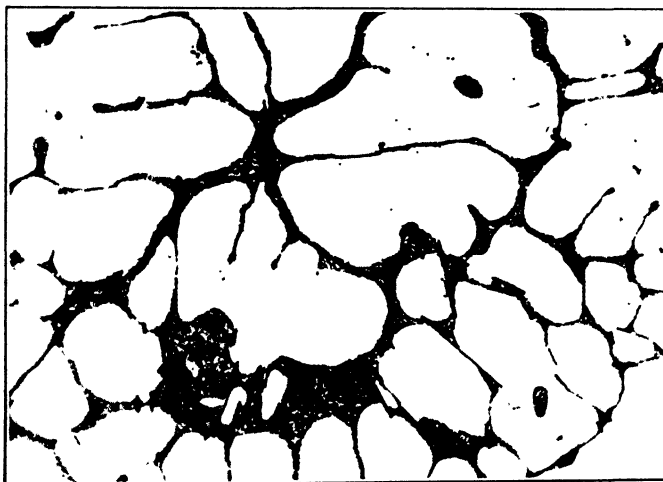


FIG. 30.—MODIFIED ALLOY CONTAINING 2.75 PER CENT. SILICON AND 0.44 PER CENT. IRON. SAMPLE 4036. ETCHED DEEPLY WITH CONCENTRATED HF. $\times 100$. THE IRON CONSTITUENT APPEARS AS DARK LINES IN THE EUTECTIC AREAS.

cast test bars made from the aluminum ingot (0.29 per cent. silicon) to a maximum of about 22,000 lb. per sq. in. for an alloy containing approximately 11 per cent. silicon, after which it decreases to about 18,000 lb.

per sq. in. at 14 per cent. silicon. The maximum strength seems to occur at approximately the composition of the normal eutectic (11.6 per cent. silicon). The decrease of strength as the silicon rises above this point is undoubtedly due to the appearance of large particles of excess silicon and the consequent embrittlement of the alloys.

The elongation of the normal alloys drops rapidly from 25 per cent. for the ingot to 10 per cent. at about 2 per cent. silicon, then more slowly as the silicon content increases. There appears, however, to be a slight maximum in the elongation curve at about 11 per cent. silicon; that is, at the normal eutectic. As the silicon rises above the eutectic proportion, the elongation decreases even more rapidly than the tensile strength, due again to the appearance of large particles of the hard and brittle primary silicon.

Turning to the modified alloys, it will be noted first that for all compositions both strength and elongation are higher than in the corresponding normal alloys. In the single experiment that was carried out, it was found that even the ingot aluminum was slightly improved by the addition of sodium. Since microscopic examination failed to reveal any free silicon in this material, the effect can scarcely be ascribed to modification in the usual sense. In all of the other alloys free silicon is present and is distinctly refined by the addition of sodium.

In the modified alloys the strength increases continuously with the silicon content to a maximum which occurs at about 13.6 to 14.1 per cent. silicon. As was shown above, this corresponds approximately to the composition of the "modified eutectic," that is, to the composition which in the fully modified condition shows neither aluminum dendrites nor primary silicon.

As in the case of the normal alloys, the elongation of the modified alloys falls rapidly as the silicon is increased from 0.29 to about 2 per cent. Further increase of silicon up to about 13 per cent. does not seem to have a marked effect on the elongation of the modified alloys. The results of the various experiments on alloys in this range of composition are not sufficiently consistent or numerous to determine the elongation curve with certainty. There seems to be a tendency for the elongation to pass through a minimum, perhaps at about 8 to 10 per cent. silicon.

As the composition approaches that of the modified eutectic there is a definite increase in elongation, and it will be noted that the elongation values obtained on alloys containing about 13.25 to 14.0 per cent. silicon are very consistent. The highest value recorded is 15.5 per cent. elongation, obtained with 14.06 per cent. silicon. Individual test bars showed elongations as high as 17.5 per cent.

Both the strength and the elongation of the modified alloys decrease rapidly as the silicon content is increased above that of the modified eutectic. This is due not only to the appearance of relatively large

particles of primary silicon but also to the fact that the eutectic areas are no longer uniformly refined.

In these experiments the silicon content was carried only slightly past the points at which the properties of the normal and modified alloys begin to decrease. It is known from many other experiments that the deterioration in strength and elongation continue as the silicon content is further increased.

The preceding discussion refers entirely to the alloys in which the iron content was kept constant at about 0.35 per cent.

Referring now to Table 6 and Fig. 11, it will be seen that as the iron content of the alloys studied increases above 0.35 per cent. the elongation decreases. The strength increases at first, up to an iron content of about 0.7 to 0.8 per cent., and then decreases. With this decrease of tensile strength, the decrease of elongation becomes especially rapid.

The addition of iron to normal alloys produces somewhat similar effects; that is, decreased elongation and, eventually, decreased strength. The strength is at first increased, as in the modified alloys. In the normal alloys the detrimental effect of iron is in general more marked as the silicon content increases.

It seems somewhat paradoxical, therefore, to find, as indicated by the results here given, that the detrimental effects of iron in the modified alloys (11 to 14 per cent. silicon) are slightly less as the silicon content increases. This is perhaps explained by the observation that, with a given iron content, the lower the silicon content of the alloy, the coarser the iron constituent found in the modified alloys (see Fig. 25 and discussion). The general effects of iron seem to be adequately accounted for by the structural changes illustrated in Figs. 22 to 29. It is known that the harmful effects of iron in the alloys containing around 13 per cent. silicon rapidly increase as the iron content rises above 1.0 per cent. With higher iron content it does not appear possible, by the use of sodium, to keep the iron constituent from becoming very coarse. In alloys containing large amounts of iron, say over 1.0 per cent., it is quite likely that again the effect of iron is relatively more harmful as the silicon content increases, as has been found in the normal alloys.⁷

The discovery that the amount of sodium required to produce maximum physical properties varies over a wide range as the silicon content of the alloy increases, as shown in Fig. 12, is obviously of great practical

⁷ It has been observed in some cases that when the iron content of modified alloys begins to exceed the amount that gives maximum tensile strength, the iron constituent begins to appear in the primary aluminum areas as well as in the eutectic areas. This indicates that the coarsening of the iron constituent and the consequent rapid deterioration of physical properties are due to the fact that the iron content has exceeded that of the ternary (or more complex) eutectic, thereby causing the iron constituent to form at higher temperatures.

importance, and is of considerable theoretical interest as well. Referring to the curve, it will be noted that the amount of sodium added increases from about 0.01 per cent. for the aluminum ingot to about 0.06 per cent. at the composition of the normal eutectic, 11 to 12 per cent. silicon. As the silicon content increases from this point to that of the modified eutectic, the sodium requirement rises rapidly from 0.06 to about 0.10 per cent. Beyond this point, still larger quantities of sodium seem to be required to produce maximum properties, although it is no longer possible to suppress completely the crystallization of excess silicon.

The rapid increase in the sodium requirement as the silicon content rises above that of the normal eutectic is apparently due to the increased difficulty of suppressing the crystallization of the primary silicon.

SOME PRACTICAL CONSIDERATIONS

The aluminum-silicon alloys possess certain advantageous properties which assure them an important place in the field of aluminum castings. Among these may be mentioned fluidity, freedom from hot shortness, freedom from leakage, and resistance to corrosion. The alloy compositions employed, the proportion used in the modified condition, and the methods of modifying will eventually be determined by extended commercial experience. A laboratory investigation, such as the one here reported, can hope only to point out the possibilities and perhaps shorten the route to the final result. It is beyond the scope of this paper to attempt a complete discussion of all the factors which even now are known to have a bearing on the practical application of these experimental results. It is felt desirable, however, to call attention to a few points which seem to the present authors to be of special importance in connection with the modified alloys, and to outline a suggested method of approaching the modifying problem.

First, it is desired to emphasize the fact that the physical properties here given are close to the maximum values for the alloys concerned. In the present state of the art, considerably lower values must be expected in average commercial practice.

Most modified castings are now made of an alloy containing on the average about 12.75 per cent. silicon. The selection of this composition seems to be based on a demand for the best combination of tensile strength and elongation. For many purposes, modified alloys of considerably lower silicon content would probably be more suitable, on account of their greater softness, plasticity, electrical conductivity, or other special property. That these alloys, in the modified condition, have been somewhat overlooked is perhaps due to lack of general knowledge that their properties can be so much improved by modification.

The greatest demand will probably continue to be for the maximum combination of strength and elongation; that is, for the properties charac-

teristic of the alloys containing about 13 per cent. silicon. It has here been shown that both strength and elongation reach maximum values at or slightly below the composition of the modified eutectic, say at 13.25 to 14.0 per cent. silicon. This does not necessarily mean, however, that the adoption of this range of composition would insure maximum properties in commercial castings.

In the first place, it is commercially difficult to control composition within such close limits. It has been shown that as the silicon content exceeds the upper limit both strength and elongation fall off rapidly. A decrease of silicon content below the lower limit mentioned causes a much more gradual decrease in strength and elongation. Therefore it is safer to work towards the lower side of the optimum silicon content.

Secondly, it is desirable to keep in mind the possible effects of imperfect modification. The properties of the normal alloys begin to decrease as the silicon content rises above 11 to 12 per cent. and are distinctly inferior at 13.25 to 14.0 per cent. silicon. The possibility of failing to obtain complete modification, therefore, indicates the use of less than the theoretical optimum silicon content. With good foundry control and perhaps with increased technical knowledge, it may prove desirable to attempt to take advantage of the superior properties of the alloys with compositions close to that of the modified eutectic.

The fact that the amount of sodium required to produce maximum properties varies with the silicon content (and perhaps with other characteristics) of the alloy indicates the desirability of basing commercial production of modified castings on large lots of uniform alloy. Having obtained a large quantity of suitable material, a few preliminary experiments may be carried out to fix the details of the modifying process in accordance with conditions in the foundry and, perhaps, the requirements of the particular job to be run.

Suppose the castings to be made are such that a pouring temperature of 693° C. (1280° F.) is suitable, and that the size of the castings and the foundry equipment indicate a pouring crucible or ladle of 100-lb. capacity. The temperature of the metal at the time of adding sodium and the temperature to which the pouring crucible is preheated may then be determined by experiment so that the metal will reach the desired pouring temperature in 5 to 25 (preferably 10 to 20) min., remembering that it is desirable to keep the modifying temperature under about 788° C. (1450° F.). Suppose it is found that with a modifying temperature of 760° C. (1400° F.) and with the pouring crucible preheated to a dull red, the metal cools to the right pouring temperature in about 12 min. A few experiments with various amounts of sodium will indicate the best quantity to use under the conditions adopted. An attempt should then be made in regular practice to adhere as closely as possible to all details of the procedure thus determined. With a little experience, it is often

possible to tell from the fracture of the metal whether it is properly modified, under-modified (too little sodium) or over-modified (too much sodium).

SUMMARY

Results are given of an investigation of the effects of silicon content and iron content on the tensile properties of sand-cast aluminum-silicon alloys modified by the addition of sodium to the melt shortly before casting. The modifying process is discussed in detail and some suggestions are made for the practical operation of this process. The tensile properties are also given for a series of normal sand-cast aluminum-silicon alloys.

The more important results are summarized in the following statements. The values given for the strength and elongation of the modified alloys are not average values but nearly maximum values of well modified sand-cast test bars $\frac{1}{2}$ in. in diameter. The alloys under consideration contain less than 0.05 per cent. each of copper and manganese.

1. Metallic sodium produces as good and as uniform modification as the salt flux, and is distinctly more economical.

2. The chief requirement for good modification is that the molten alloy contain a certain definite amount of sodium at the moment of casting. Larger or smaller amounts give inferior results.

3. The amount of sodium required for modification varies with the silicon content, and perhaps with other characteristics, of the alloy to be modified. The amount of sodium added to produce good modification, under the specific conditions here employed, varies from about 0.01 per cent. for an alloy containing less than 1 per cent. silicon to about 0.10 per cent. for an alloy containing 14 per cent. silicon.

4. For sand castings $\frac{1}{2}$ in. thick modified with sodium, the modified "eutectic" occurs at about 14.0 per cent. silicon.

5. The tensile strength of the normal alloys increases with silicon content from 12,800 lb. per sq. in. for the aluminum ingot used to about 22,000 lb. per sq. in. at the composition of the normal eutectic (11 to 12 per cent. silicon), and then decreases rapidly with further additions of silicon. This applies to alloys containing 0.35 per cent. iron.

6. The elongation of the normal alloys decreases rapidly from 25 per cent. for the ingot to 10 per cent. at about 2 per cent. silicon, then more slowly as the silicon increases. There is apparently a slight maximum of about 5 to 6 per cent. elongation at the composition of the normal eutectic. Further additions of silicon cause the elongation to decrease rapidly to less than 2 per cent. at 14 per cent. silicon.

7. For all compositions both strength and elongation are improved by modification.

8. The tensile strength of the modified alloys (0.35 per cent. iron) increases with silicon content to a maximum of 27,000 to 28,000 lb. per

sq. in. at the composition of the modified eutectic (14 per cent. silicon) then decreases with further additions of silicon.

9. The elongation of the modified alloys decreases from 28 per cent. for the ingot to about 13 per cent. at 1.5 per cent. silicon, remains nearly constant to about 12 per cent. silicon, rises slightly at the composition of the modified eutectic (14 per cent. silicon), and then falls rapidly with higher amounts of silicon.

10. The addition of iron above 0.35 per cent. to the modified alloys decreases elongation.

11. The addition of iron above 0.35 per cent. to the modified alloys containing 11 to 14 per cent. silicon increases tensile strength up to about 0.75 per cent. iron; further additions of iron decrease tensile strength as well as elongation.

12. The alloy compositions which give the maximum properties when properly modified are not necessarily those which will consistently give the best average results in commercial practice.

DISCUSSION

J. L. JONES, Pittsburgh, Pa.—In the case of a quite large casting (say, one weighing 2500 lb.) would any more difficulty be experienced in meeting the U. S. Navy specification of 25,000 tensile strength and 8 per cent. elongation, than would be had in the case of a small casting, both being cast from the 13 per cent. silicon alloy?

F. B. COYLE, New York, N. Y.—At the Brooklyn Navy Yard modified aluminum-silicon alloy castings containing 13 per cent. silicon up to 350 lb. weight each have been manufactured. Until about a year or so ago no difficulty was encountered in meeting the Navy specification, but more recently we have had quite a bit of difficulty in meeting the 8 per cent. requirement for elongation. In discussing this there were two questions which arose: What was the iron content and what was the copper content?

The results in the paper just read show the iron is low, 0.35 per cent. The Navy specification allows a maximum of 0.60 per cent. The copper in the results given today was maximum 0.04 per cent. The Navy specification permits 0.60 per cent. on the 13 per cent. silicon type. About a year and a half ago the castings manufactured at the Brooklyn Navy Yard would run around 0.40 per cent. iron and 0.20 per cent. copper, and no difficulty was experienced. Some results were as high as 13½ per cent. elongation. We had no difficulty whatever with the tensile strength, but in the last year some of the material delivered—the original ingot—contained as high as 0.70 per cent. iron. Some ingots in the same lot would be about 0.85 per cent.; the average would be just about

0.58 per cent. The result was that some lots of castings were obtained containing a bit over the maximum, 0.60 per cent., which would cause the elongation to be low.

Perhaps the author can present some more information about the effect of copper in excess of 0.40 per cent., with iron in excess of 0.50 per cent.

Another point I would like to ask in regard to the Navy specification is: Would it be advisable to lower the limit of iron to 0.50 per cent., and would it be possible to lower the content of copper, and to what extent, and what effect would it have upon the price of the original material?

R. S. ARCHER.—The main problem in getting Navy specification properties on a 2500-lb. casting is that of modification. Presumably the test bars would still be cast in the small mold, so there is no question of section thickness; it is a question of modifying a large quantity of metal. The largest amount of metal that we have ever modified at one time was 900 lb. We did that by melting in a brick-lined furnace and tapping into a 900-lb. ladle, throwing in the sodium from time to time during the tapping. Possibly there were six additions during that time. We only ran one experiment of this kind, and it happened that we got excellent physical properties, so we know it can be done, but we have not done it on a commercial scale. To pour your 2500-lb. casting would require, ordinarily, about four such ladles, and you would have to modify them separately or else have a much larger ladle, and in general I would say it could be done but it would probably be more difficult than handling the metal on a smaller scale.

We are investigating the effect of copper content, as well as that of other elements, such as manganese, and we hope to present these results in detail some time. They are not yet sufficiently complete for presentation. However, I believe very little of the silicon alloy marketed by the Aluminum Co. of America now contains as much as 0.2 per cent. of copper, and very little of it contains over 0.5 per cent. of iron, so that the copper content is ordinarily running closer to 0.1 per cent. The nominal specification of the ingot has 0.6 per cent. iron as a maximum, but I think that it is being kept under 0.5 per cent.

E. J. DECKER, Philadelphia, Pa.—In your modified alloy do you use any kind of a clarifier, such as sodium chloride, for cleansing?

R. S. ARCHER.—No, when we use the sodium we use no flux at all. As a matter of general practice, we find that when the metal is new and clean, the use of any kind of flux is apt to be more harmful than beneficial; that is, outside of this special flux which is designed to produce sodium.

F. B. COYLE.—I will answer the question about the size of the casting more fully. The casting was an air-cooler body for a 1750-hp. Diesel

engine. The overall dimensions were about 18 by 24 by 40 in.; there were two sections each of that size cast together, making practically one casting. The average wall thickness was about $\frac{5}{8}$ inch.

MEMBER.— What is the effect of annealing all eutectic analysis?

R. S. ARCHER.— The principal effect of annealing the modified castings consists in the spheroidizing of the silicon particles, a process of particle growth strictly analogous to the spheroidizing of cementite in steel; the particles become larger and more rounded. This is accompanied by a decrease in tensile strength and an increase in elongation.

MEMBER.— What is the status of the line *B.C.* on the equilibrium diagram?

R. S. ARCHER.— This diagram, as I mentioned, is one in which the dotted lines do not even represent metastable equilibrium. It is a strictly unstable condition, there is no equilibrium to it. It is a condition of undercooling, and the thermodynamic considerations of the phase rule and other fundamental principles do not apply at all, any more than they do in a system which is undercooled by rapid cooling. Actually, the silicon is in a condition of greater free energy simply because the particles are much smaller and therefore present more surface.

The theory is gone into in some detail in this paper, and references are given to papers in which it is discussed in greater detail.

The Microstructure of Aluminum

BY K. L. MEISSNER, BERLIN, GERMANY

(New York Meeting, February, 1926)

IT IS well known that the so-called pure aluminum contains noticeable amounts of impurities, chiefly iron and silicon, and many investigators have studied the forms in which these impurities exist. Hanson and Archbutt¹ state that iron exists in aluminum as FeAl_3 and silicon as elementary Si. The solubility of FeAl_3 in solid aluminum is practically zero, or at least so small that the smallest trace of this compound is always visible as a separate constituent. Under the microscope an untrained eye can hardly distinguish, without etching, the two constituents FeAl_3 and Si, but they can be differentiated by suitable etching reagents. Anderson² also found the same results.

At the same time, Merica, Waltenberg, and Freeman³ found a constituent of unknown composition. They found a small thermal effect, at 610°C ., on the cooling curves of aluminum with small amounts of iron and silicon. The intensity of this effect increased with increasing silicon content, until an effect occurred at 576°C . due to the eutectic between aluminum and silicon. The authors ascribed the effect at 610°C . to a compound, which they call "X constituent." It was thought to be a ternary compound containing iron and silicon and could be observed under the microscope as dark particles.

Dix⁴ has published unetched photomicrographs of an aluminum with 0.51 per cent. iron, 0.99 per cent. silicon, and 0.32 per cent. copper that shows three constituents: the dark Si (black in the figure), the lighter FeAl_3 , which appears in half tone and crystallizes in needles, and a constituent of the same color as FeAl_3 but of different crystal form, often resembling Chinese script. This last constituent, Dix thought, is a compound of Fe and Si; not the compound FeSi but a compound containing a relatively small amount of silicon. Therefore an alloy of aluminum, iron, and silicon (the copper should not be regarded in the following considerations) must contain the following four constituents: Al, FeAl_3 , Si, and a compound of Fe and Si. This, however, does not agree with the laws of chemical equilibrium.

¹ *Jnl. Inst. of Metals* (1919) **21**, 291.

² *Chem. & Met. Eng.* (1919) **21**, 229.

³ *Trans.* (1919) **64**, 3; *Bur. Standard Sci. Paper No. 337* (1919).

⁴ *Chem. & Met. Eng.* (1922) **27**, 1217; (1923) **28**, 392.

In this paper a method of research originated by Guertler,⁵ and first applied by the author,⁶ for determining the equilibrium conditions in a number of ternary metal systems, is used in an effort to explain this problem.

In Fig. 1 the ternary system Al-Fe-Si is shown, each angle representing one constituent as 100 per cent. The three sides signify the binary alloys Al-Fe, Al-Si, and Fe-Si. As only the aluminum-rich part of the diagram is of interest, on the Al-Fe axis there is shown only the compound richest in aluminum, FeAl_3 . Similarly on the Fe-Si axis only the compound FeSi is marked. The third binary system, Al-Si, forms a simple eutectiferous series⁷ without any compound; hence on this axis no point is indicated. Within the triangle area, every composition containing the metallographic constituents of the three elements can be marked.

To determine all the possible alloys of aluminum, iron, and silicon *i. e.*, to determine whether in a certain composition the constituents Al, FeAl_3 , Si, FeSi , etc. can exist, join the points corresponding to the three elements and both compounds, FeAl_3 and FeSi as shown in Fig. 1. The lines Al- FeSi and FeAl_3 -Si thus drawn cross at the point *K*. According to the laws of chemical equilibrium, only on these junction lines can alloys containing no more than two constituents exist. When two such lines cross as in the present system, the question arises, which of the two lines corresponds to a "quasi-binary" alloy system; that is, to a system containing the two constituents indicated at the ends of these lines. In the present case, it is a question whether the alloy corresponding to the point *K* consists of a mixture of Al and FeSi , or of FeAl_3 and Si. All four constituents Al, FeAl_3 , Si, and FeSi cannot occur simultaneously, because, in a mixture of three elements, and at a certain temperature, no more than three constituents can be in equilibrium together. Even three constituents, however, cannot exist at the point *K*, because it is impossible to produce by three constituents the mixture corresponding to the point *K*. Thus by mixing the two constituents FeAl_3 and Si, the only result is a composition lying on the direct junction line between the two. Any addition of another constituent, for example Al, removes the composition of the final alloy from the direct line FeAl_3 -Si, to which the point *K* belongs.

For the present system Al-Fe-Si, it has been shown in the investigation by Fuss,⁸ carried out under the direction of Professor Guertler, that the line FeAl_3 -Si corresponds to a real quasi-binary alloy system;

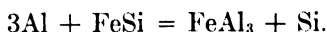
⁵ *Metall und Erz* (1920) 192.

⁶ *Metall und Erz* (1921) 145, 358, 410, 438, 466; *Zeit. Metallkunde* (1922) 173.

⁷ W. Fraenkel; *Zeit. anorg. Chemie.* (1908) 58, 154.

⁸ *Zeit. Metallkunde* (1924) 16, 24.

therefore, the line Al-FeSi must be omitted from the triangle diagram. In other words, mixtures of Al and FeSi cannot be melted together in any composition, but they must react by turning into other constituents. For example, in the point *K* this reaction follows to the formula:



In the space between Al and *K*, aluminum is in excess; hence this reaction goes on until all FeSi has disappeared. After equilibrium is reached, the constituents Al, FeAl₃, and Si exist in the alloy. Similarly, in the space between the points *K* and FeSi there is an excess of FeSi. In such alloys, therefore, the reaction goes on until all the elementary aluminum has disappeared.

The foregoing considerations are based on the presumption that no ternary compound exists in the system. In the investigation of Fuss,

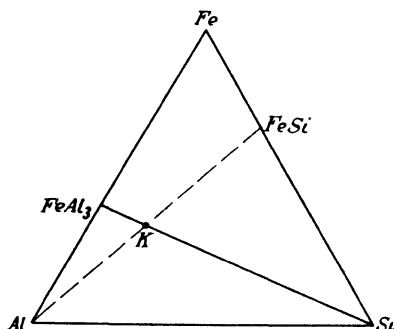


FIG. 1.

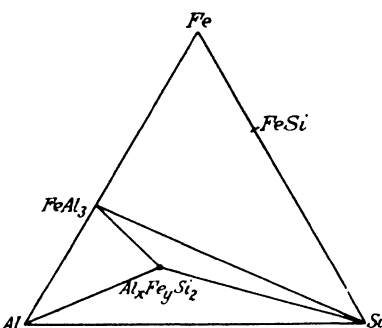


FIG. 2

no compound of that kind has been found. Nevertheless, the possibility of one or even several ternary compounds existing must be considered; to which possibility the various constituents of unknown identity mentioned by Dix, and the thermal effect at 610° C. found by Merica and his associates, seem to point. It follows that, with the occurrence of even one ternary compound, new real sections (*i. e.*, sections corresponding to quasi-binary alloy systems) and simultaneous new partial triangles must result in the ternary system Al-Fe-Si. It is also evident that such a ternary compound, if it exists at all, can lie only in the triangle of the system limited by the constituents Al, FeAl₃, and Si, or on the line FeAl₃-Si itself, at least. Then, it is just as impossible for a compound of a composition lying outside of the triangle Al-FeAl₃-Si to be found in the microstructure of the aluminum as it is for the compound FeSi or any other Fe-Si compound. The section FeAl₃-Si, which is demonstrated to be real, makes it impossible for other constituents to exist in the aluminum-rich corner of the system Al, FeAl₃, and Si.

Assuming, now, the existence of a ternary compound $\text{Al}_x\text{Fe}_y\text{Si}_z$ in the triangle $\text{Al-FeAl}_3\text{-Si}$, its position in the diagram corresponding to the simple molecular proportions, the partial triangle $\text{Al-FeAl}_3\text{-Si}$, Fig. 2, will be divided into three systems. Within these systems only the constituents can exist that are indicated at the corners of each triangle. That means, for example, an alloy or an aluminum that, according to the amount of its impurities Fe and Si, lies in the triangle $\text{Al-FeAl}_3\text{-Al}_x\text{Fe}_y\text{Si}_z$, can contain only FeAl_3 and the ternary compound besides the aluminum matrix.

Now Dix mentions an aluminum with 0.63 per cent. iron and 0.63 per cent. silicon, the photomicrograph of which shows needles of FeAl_3 and the X constituent resembling "Chinese script," but no silicon is seen. He also states that, with increasing silicon content, all the Fe is contained in the X constituent, no more FeAl_3 being found. In other words, the composition of the alloy, with increasing silicon content, has

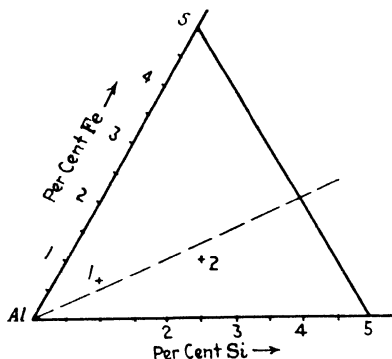


FIG. 3.

passed over from the triangle $\text{Al-FeAl}_3\text{-Al}_x\text{Fe}_y\text{Si}_z$ to the triangle $\text{Al-Al}_x\text{Fe}_y\text{Si}_z\text{-Si}$, where only these constituents can exist, and not the compound FeAl_3 . This agrees with the statement of Merica that, at first, from a certain higher silicon content a thermal effect on the cooling curves is found at 576°C ., due to the eutectic between aluminum and silicon. Thence it results that, at first, these alloys of the higher silicon content mentioned would lie with their composition in the triangle $\text{Al-Al}_x\text{Fe}_y\text{Si}_z\text{-Si}$, to which also the eutectic point between aluminum and silicon belongs. With an aluminum of 1.0 per cent. iron and 2.0 per cent. silicon, mentioned by Dix, all FeAl_3 has disappeared. There occurs the X constituent and elementary silicon, and another unknown constituent, which seems to be found only by equilibrium troubles. Dix writes that it would probably disappear by annealing, only the reaction goes on very slowly.

In Fig. 3 is shown the aluminum-rich corner of the ternary system Al-Fe-Si on an enlarged scale, and with the positions of the two alloys

with 0.63 per cent. iron and 0.63 per cent. silicon (point 1) and with 1.0 per cent. iron and 2.0 silicon (point 2) marked. The quasi-binary section $\text{Al}-\text{Al}_x\text{Fe}_y\text{Si}_z$ must, according to the microstructure given by Dix, pass between the points 1 and 2, as shown by the dotted line; that is, the position of the compound $\text{Al}_x\text{Fe}_y\text{Si}_z$ or of the X constituent (Merica) must be looked for near this line.

Other problems have prevented the author from performing this investigation himself. He hopes, however, that he has given a suggestion for further experiments, which will give a final explanation of the riddles still existing in the microstructure of aluminum.

DISCUSSION

E. H. DIX, Jr., New Kensington, Pa.—The title, "The Microstructure of Aluminum," is misleading and will probably cause confusion in references. I notice that Dr. Meissner has referred to some of my discussions. I have not had opportunity to look up the exact wording of my paper that he refers to on the first page, but have a feeling that at that time I was careful not to say that the "x" constituent was a compound of iron, silicon and aluminum. I know that I was rather specific that it was not the compound FeSi .

Since that time I have had evidence of an indirect nature, which strengthens my feeling that the "x" constituent is not a definite compound of iron, silicon and aluminum. Occasionally, in a reduction pot, the lining will break through, allowing some of the aluminum to slowly trickle down. If this happens to run over an iron re-enforcing bar, very often clumps of crystals are formed, which have very perfect exterior forms. I had the opportunity of examining three groups of these crystals. One group was composed entirely of well-formed needles, the form that we have always associated with FeAl_3 . On analysis of these needles, we found that the composition was very close to the compound FeAl_3 , as close as we could expect because of the unavoidable errors which follow from analyzing such crystals. There was very little silicon present, less than 0.5 per cent. Another group of crystals contained thin hexagonal plates. In some of the aluminum alloys containing high iron and silicon we have found these same plates in the microstructure surrounded by areas of "Chinese script," as though these hexagonal plates were a primary constituent and the "Chinese script" the eutectic formed around the primary particles. So that on analysis of these plates we were not surprised to find an appreciable quantity of silicon. The analysis showed in the neighborhood of 12 to 15 per cent. of both iron and silicon, the balance aluminum.

I was elated at finding this and I said, "Here we have trapped the 'x' constituent at last." We made up some alloy of that composition and we

found the microstructure to consist of iron needles and free silicon, scattered through a matrix of aluminum. On annealing for a considerable length of time at a high temperature, these particles did tend to take the form of hexagonal plates, and from this alone we would have been inclined to feel that perhaps there was a definite compound. However, a few months later we found another group of these crystals, very similar in appearance. On analysis, the ratio of the iron, silicon and aluminum was entirely different, which I believe indicates that there is not a definite compound. There is a reaction between the three to form a constituent, but not a definite compound.

This whole method seems to be based on the fact that there is a definite ternary compound formed. It appears to me that the assumptions necessary to apply this method are more difficult than would seem from reading the paper. Reference is made to the investigation by Fuss. I was rather disappointed when I looked it up. It was a paper of perhaps 3 or 4 pages, and in it there was possibly 15 systems mapped out. It would not be wise to depend very much on such very slight evidence.

The Relation between Metallurgy and Atomic Structure*

BY PAUL D. FOOTE,† WASHINGTON, D. C.

(New York Meeting, February, 1926)

MOST of the treatises on metallurgy intimate that simultaneously with the development by the atomic physicist of a really satisfactory theory of the atom will be inaugurated a new epoch in the science of metals. Metallurgically and metaphorically, we shall dwell in the Utopia of Sir Thomas More. It is my privilege this afternoon to demonstrate that this state has not arrived.

An atom is a miniature planetary system consisting of a positively charged nuclear sun about which revolve electrons each carrying the negative charge e . The charge on the nucleus is $+Ze$ where Z is the atomic number and the number of planetary electrons in a neutral atom is equal to Z . These electrons are arranged in several groups having different binding energies. Ordinary x -ray phenomena relate to processes occurring deep within the atom, usually with electrons in the so-called K or L shells. Such electrons in the heavier atoms are so closely bound to the nucleus that the forces exerted by neighboring atoms in a solid are relatively inappreciable. For most practical x -ray investigation, the atom may be considered as in the gaseous phase completely isolated from its neighbors. The K radiation from an element in the gaseous state, in the solid or liquid phase, or even in combination with other elements in all its possible valences, is almost identical.‡

Visual and ultraviolet spectroscopy is concerned with disturbances of the most loosely bound outer or valence electrons of the atom, always in the vapor state. The remarkable progress of the last year in both theo-

* Presented in synopsis as the Fifth Annual Lecture of the Institute of Metals Division, the American Institute of Mining and Metallurgical Engineers, at the New York Meeting, February, 1926. Published by permission of the Director of the Bureau of Standards, Department of Commerce.

† Physicist, Bureau of Standards.

‡ Small variations in the K limit of a light element such as sulfur, amounting to a few parts in 5000, have been detected. The interpretation of such deviations as related to the atomic and molecular structure has not been developed, but it is quite possible that valuable information may be eventually derived from investigation of this type, especially with the softer lines and limits.¹

retical and experimental spectroscopy has yielded an immense amount of information regarding the behavior of any isolated atom but almost nothing of direct application to the solid phase.

Up to the present time the subject of atomic structure has been primarily devoted to the investigation of the outer groups of electrons of atoms in the vapor phase (conductivity of electricity through gases and vapors and spectroscopic phenomena); to the study of the inner electron groups which are ineffective chemically and in general physically (*x*-rays); and, finally, to experimentation upon the nuclear sun, the precise structure of which plays no direct role in a theory of the solid state (radioactivity and atomic disintegration).

The science of metallurgy is concerned essentially with the solid or liquid phases of matter, with the properties of atomic clusters forming molecular compounds and crystals. Most of these properties are mainly due to the outer group of electrons in an atom. When the atoms are closely packed as in the solid or liquid states, serious distortions occur. The outer structure of an atom or molecule in the vapor is quite different from that in the solid.

It is therefore very difficult to make quantitative predictions for the behavior of a solid from theoretical and experimental observations on the isolated or vapor atom. Ultimately, no doubt, the *x*-ray and ultraviolet technique will be so developed that the comparatively inaccessible spectral region comprising the far ultraviolet will have been completely explored. We shall then possess data which should be useful in the theory of the solid state. In spite of the present temporary difficulties the paths of the metallurgist and atomic physicist are tending to converge, possibly in the field of crystallography. You are familiar with the developments from the metallurgical standpoint. I shall, therefore, attempt to describe in a very general way recent progress in certain phases of atomic physics which appear to offer possibilities for the extension of our conceptions of the isolated atom to the solid and liquid states of matter.

THE QUANTUM THEORY OF ATOMIC STRUCTURE

While we conceive of the atom as a planetary system of electrons, it is not entirely subject to the classical dynamic laws of ordinary celestial mechanics and electrodynamics. We have in the atom a kind of stability which is unknown in the classical mechanics. The fact that all atoms of a given species are exactly alike as determined by the most precise measurements; the fact that an atom is able to radiate a nearly monochromatic frequency instead of a spectral band, and that all atoms of the same species may emit precisely the same frequency, whether upon

this earth or a distant star, are only the more astounding the longer one considers its philosophical aspect. For these and many other reasons we have been forced to adopt a new kind of mechanics, the quantum theory of spectroscopy and atomic structure.²

According to the ordinary mechanics the electrons of an atom might revolve in a great variety of orbits, under the influence of the inverse square law of force between each pair of particles, so that various atoms of a given element should be quite different in their properties. A fundamental postulate of the quantum theory of atomic structure requires that the electrons move on a discrete set of orbits chosen by the application of equations which are known as the quantum conditions. These equations state that certain quantities characterizing the motion must be equal to integral multiples of Planck's constant h . The physical reason for this is unknown; its only justification lies in the precise experimental confirmation of numerous facts to which such an assumption leads. In the hydrogen atom, for example, we have a single electron revolving about a nucleus with unit positive charge. The motion of this electron is restricted to circular and elliptical orbits of such shape and size that 2π times its angular momentum is $n\hbar$ where n is an integer. The possible configurations complying with this condition are called stationary states because no radiation is emitted while the atom remains in such a state. Ordinarily it exists only in the stationary state of lowest energy but by absorption of radiation or by collision of certain types it may pass to an "excited" state of higher energy. Radiation is emitted during a transition from an excited state to a state of lower energy. The energy ϵ lost in the transition is conserved as radiation of frequency ν according to the simple but fundamental quantum relation $\epsilon = h\nu$. Thus observations on the radiation emitted by an atom furnish immediate information relative to the differences in energy of its various stationary states.

The most striking characteristic of the quantum theory of atomic structure is the frequent occurrence of integers and half integers; it is essentially a theory of numbers which are combined in all possible ways. The types of elliptical orbit upon which the electrons in the complicated atoms revolve may be characterized by quantum numbers n, k, k' . The number n is related to the size of the orbit, k to its shape and k' to its position in the atom relative to the other electronic orbits. For convenience a particular orbit is referred to by the notation $n_{kk'}$. The larger the value of n , the more loosely is the electron bound to the atom. The electrons may be grouped according to their values of n . For $n = 1$ we have the *K* shell effective in the hardest x -rays. The *L* shell is designated by $n = 2$ and so on for the *M*, *N*, *O* etc, shells. Table 1 shows the complete arrangement of the electrons in the 92 elements.

TABLE 1.—*Arrangement of Electrons in Atoms*

Period	Z	Element	Spectroscopic Term	Number of Electrons in Shell of Quantum Number n_{ab}											
				K_{111}	L_{11} 2_{11}	L_{11} 2_{11}	L_{111} 2_{11}	M_{11} 3_{11}	M_{11} 3_{11}	M_{111} 3_{11}	M_{11} 3_{11}	M_{11} 3_{11}	N_{11} 4_{11}	N_{11} 4_{11}	N_{111} 4_{11}
1	1	H		1											
	2	He	$1S_0$	2											
2	3	Li	$1S_{1/2}$	2	1										
	4	Be	$1S_0$	2	2										
	5	B	$1P_{1/2}$	2	2	1									
	6	C	$1P_1$	2	2	2									
	7	N	$1S_{3/2}$	2	2	2	1								
	8	O	$1P_1$	2	2	2	2								
	9	F	$1P_{3/2}$	2	2	2	3								
	10	Ne	$1S_0$	2	2	2	4								
3	11	Na	$1S_{1/2}$	2	2	2	4	1							
	12	Mg	$1S_0$	2	2	2	4	2							
	13	Al	$1P_{1/2}$	2	2	2	4	2	1						
	14	Si	$1P_1$	2	2	2	4	2	2						
	15	P	$1S_{3/2}$	2	2	2	4	2	2	1					
	16	S	$1P_1$	2	2	2	4	2	2	2					
	17	Cl	$1P_{3/2}$	2	2	2	4	2	2	3					
	18	A	$1S_0$	2	2	2	4	2	2	4					
4	19	K	$1S_{1/2}$	2	2	2	4	2	2	4			1		
	20	Ca	$1S_0$	2	2	2	4	2	2	4			2		
	21	Sc	$1D_{3/2}$	2	2	2	4	2	2	4	1		2		
	22	Ti	$1F_1$	2	2	2	4	2	2	4	2		2		
	23	V	$1F_{3/2}$	2	2	2	4	2	2	4	3		2		
	24	Cr	$1S_{1/2}$	2	2	2	4	2	2	4	4	1	1		
	25	Mn	$1S_{3/2}$	2	2	2	4	2	2	4	4	1	2		
	26	Fe	$1D_1$	2	2	2	4	2	2	4	4	2	2		
	27	Co	$1F_{5/2}$	2	2	2	4	2	2	4	4	3	2		
	28	Ni	$1F_1$	2	2	2	4	2	2	4	4	4	2		
	29	Cu	$1S_{1/2}$	2	2	2	4	2	2	4	4	6	1		
	30	Zn	$1S_0$	2	2	2	4	2	2	4	4	6	2		
	31	Ga	$1P_{1/2}$	2	2	2	4	2	2	4	4	6	2	1	
	32	Ge	$1P_1$	2	2	2	4	2	2	4	4	6	2	2	
	33	As	$1S_{3/2}$	2	2	2	4	2	2	4	4	6	2	2	1
	34	Se	$1P_1$	2	2	2	4	2	2	4	4	6	2	2	2
	35	Br	$1P_{3/2}$	2	2	2	4	2	2	4	4	6	2	2	3
	36	Kr	$1S_0$	2	2	2	4	2	2	4	4	6	2	2	4

TABLE 1.—*Arrangement of Electrons in Atoms—(Continued)**K, L, and M Shells Like Kr Complete with 28 Electrons*

Period	Z	Element	Spectroscopic Term	Number of Electrons in Shell of Quantum Number n_{kl}											
				N_I 4 ₁₁	N_{II} 4 ₂₁	N_{III} 4 ₃₁	N_{IV} 4 ₄₁	N_V 4 ₅₁	N_{VI} 4 ₆₁	N_{VII} 4 ₇₁	O_I 5 ₁₁	O_{II} 5 ₂₁	O_{III} 5 ₃₁	O_{IV} 5 ₄₁	P_I 6 ₁₁
5	37	Rb	$^1S_{1/2}$	2	2	4						1			
	38	Sr	1S_0	2	2	4						2			
	39	Y	$^2D_{3/2}$	2	2	4	1					2			
	40	Zr	1F_3	2	2	4	2					2			
	41	Cb	$^2D_{3/2}$	2	2	4	4					1			
	42	Mo	1S_0	2	2	4	4	1				1			
	43	Ma	$^2D_{3/2}$	2	2	4	4	(2)			(1)				
	44	Ru	3F_4	2	2	4	4	3				1			
	45	Rh	$^4F_{9/2}$	2	2	4	4	4				1			
	46	Pd	1S_0	2	2	4	4	6							
	47	Ag	$^2S_{1/2}$	2	2	4	4	6				1			
	48	Cd	1S_0	2	2	4	4	6				2			
	49	In	$^2P_{1/2}$	2	2	4	4	6				2	1		
	50	Sn	1P_0	2	2	4	4	6				2	2		
51	Sb	$^3S_{3/2}$	2	2	4	4	6				2	2	1		
52	Te	1P_1	2	2	4	4	6				2	2	2		
53	I	$^2P_{3/2}$	2	2	4	4	6				2	2	3		
54	Xe	1S_0	2	2	4	4	6				2	2	4		
6	55	Ce	$^2S_{1/2}$	2	2	4	4	6				2	2	4	1
	56	Ba	1S_0	2	2	4	4	6				2	2	4	2
	57	La	$^2D_{3/2}$	2	2	4	4	6				2	2	4	2
	58	Ce	3H_4	2	2	4	4	6	1			2	2	4	2
	59	Pr	$^4K_{11/2}$	2	2	4	4	6	2			2	2	4	2
	60	Nd	1L_6	2	2	4	4	6	3			2	2	4	2
	61		$^4L_{11/2}$	2	2	4	4	6	4			2	2	4	2
	62	Sm	1K_4	2	2	4	4	6	5			2	2	4	2
	63	Eu	$^3H_{3/2}$	2	2	4	4	6	6			2	2	4	2
	64	Gd	2D_5	2	2	4	4	6	6	1		2	2	4	2
	65	Tb	$^3H_{11/2}$	2	2	4	4	6	6	2		2	2	4	2
	66	Dy	$^1K_{10}$	2	2	4	4	6	6	3		2	2	4	2
	67	Ho	$^4L_{21/2}$	2	2	4	4	6	6	4		2	2	4	2
	68	Er	$^4L_{10}$	2	2	4	4	6	6	5		2	2	4	2
	69	Tm	$^4K_{11/2}$	2	2	4	4	6	6	6		2	2	4	2
	70	Yb	1H_6	2	2	4	4	6	6	7		2	2	4	2
	71	Lu	$^2D_{3/2}$	2	2	4	4	6	6	8		2	2	4	2

TABLE 1.—*Arrangement of Electrons in Atoms—(Continued)*
K, L, M and N Shells Like Lu Complete with 60 Electrons

Period	Z	Element	Spectroscopic Term	Number of Electrons in Shell of Quantum Number n_{sh} .									
				O_I 5 ₁₁	O_{II} 5 ₂₁	O_{III} 5 ₂₂	O_{IV} 5 ₂₃	O_V 5 ₂₄	P_I 6 ₁₁	P_{II} 6 ₂₁	P_{III} 6 ₂₂	P_{IV} 6 ₂₃	Q_I 7 ₁₁
	72	Hf	1F_3	2	2	4	2		2				
	73	Ta	$^1F_{3/2}$	2	2	4	3		2				
	74	W	1D_2	2	2	4	4		2				
	75	Re	$^1S_{3/2}$	2	2	4	4	1	2				
			$^1D_{3/2}$					2	1				
	76	Os	1D_2	2	2	4	4	2	2				
			1F_3					3	1				
	77	Ir	$^1F_{3/2}$	2	2	4	4	3	2				
			$^1F_{5/2}$					4	1				
	78	Pt	1F_4	2	2	4	4	4	2				
			1D_3					5	1				
			1S_6					6					
	79	Au	$^1S_{1/2}$	2	2	4	4	6	1				
	80	Hg	1S_6	2	2	4	4	6	2				
	81	Tl	$^1P_{1/2}$	2	2	4	4	6	2	1			
7	82	Pb	1P_2	2	2	4	4	6	2	2			
	83	Bi	$^1S_{3/2}$	2	2	4	4	6	2	2	1		
	84	Po	1P_2	2	2	4	4	6	2	2	2		
	85		$^1P_{3/2}$	2	2	4	4	6	2	2	3		
	86	Rn	1S_6	2	2	4	4	6	2	2	4		
	87		$^1S_{1/2}$	2	2	4	4	6	2	2	4		1
	88	Ra	1S_6	2	2	4	4	6	2	2	4		2
	89	Ac	$^1D_{3/2}$	2	2	4	4	6	2	2	4	(1)	(2)
	90	Th	1F_3	2	2	4	4	6	2	2	4	(2)	(2)
	91	PAc	$^1F_{3/2}$	2	2	4	4	6	2	2	4	(3)	(2)
	92	U	1D_2	2	2	4	4	6	2	2	4	(4)	(2)

The principal features of this table were derived by Stoner,² empirically, from consideration of various physical data, and by Main Smith,⁴ independently, from chemical data before its heuristic deduction by the recent work of Pauli,⁵ Heisenberg⁶ and Hund.⁷ It is an extension of the earlier suggestions made by Bohr.³ The similarity of the inner structure of the different atoms is apparent. Beginning with helium the *K* shell is completely filled by two 1₁₁ electrons for all succeeding atoms. The 2₁₁ group in the *L* shell remains permanently closed by two electrons for all elements following lithium, and so on. Any *k'* group is closed by 2*k'* electrons. This requires the closing of the *n* groups with the numerical sequences 2 + 8 + 18 + 32 which gives directly the periods of the elements. The presence of homologues is immediately indicated by their general similarity in outer structure; compare the outer structures of Li, Na, K, Rb, Cs. The chemical similarity of the triads, for example Fe, Co, Ni, and the existence of exactly 14 rare earths is a necessary requirement of the theory upon which this table is based. Indeed in all physics and chemistry there are no phenomena of direct applicability which are

inconsistent with the electronic configurations here described. Obviously to demonstrate the truth of such a statement would lead us far afield.*

X-rays arise from disturbances of the configurations in the underlying shells. For example, if a K electron is removed from the atom and an L_{II} or L_{III} electron falls to the orbit originally occupied by the K electron, we have the emission of either the $K\alpha_2$ or $K\alpha_1$ x-ray line. All the known x-ray lines may be accounted for by the use of one K absorption limit, 3 L limits, 5 M limits and 7 N limits as indicated, and as found experimentally for atoms in which these shells are closed.

When an outer or valence electron is ejected to a still further outlying orbit and then returns, it emits certain spectroscopic lines. Since these lines are concerned with transitions between various orbits which may be specified by the quantum numbers, there exists an interrelation between the spectral lines of a given atom. In the case of the alkalis, where there is a single valence electron, we have the familiar doublet spectrum containing pairs of lines which are arranged in a sequence of decreasing wave lengths. Many such series are known and the spectral term corresponding to a particular type of electronic configuration is given a name by spectroscopists. We therefore have S , P , D , F , G , H , J , K , L , etc., sequences, the character of any of which is readily recognizable by the behavior of the term when the radiating atom is in a magnetic field, *i. e.*, the Zeeman effect.¹⁰

If there is only one valence electron the spectroscopic terms belong to a doublet system. With two valence electrons, as for metals of Group II of the periodic table, we have singlet and triplet systems. The complication increases for elements with many valence electrons and spectroscopists have recently disentangled sequences belonging to quartet, quintet, sextet, septet and octet systems of certain atoms. Nearly every line in the spectrum of titanium has been classified. A few typical examples of the so-called multiplets belonging to different systems are shown in Fig. 1. The point which should be emphasized is that in these complicated spectra nature has furnished solutions of the n -body problem. Corresponding to any specified arrangement whatever of the valence electrons, we are able, by use of the formulas developed by Hund,⁷ to

* With the further accumulation of data slight changes may be necessary in this table but undoubtedly they will be of minor importance. For example two slightly different configurations are indicated for Os and three for Pt. These differ by an exceedingly small amount of energy and all are possible. Just as with the Fe and Pd triads spectroscopic data will decide which of the configurations for each element of the Pt triad represents the normal state and which are the excited states of higher energy. A few other examples of a similar nature await confirmation, especially for the elements 89 to 92. The table includes hafnium, 72 Hf, discovered by v. Hevesy and Coster⁸ in 1923, rhenium, 75 Re, and masurium, 43 Ma, discovered by Noddack and Tacke⁹ in 1925, as well as the three yet unknown elements, 61, 85 and 87. The complete spectrum of the latter may be predicted with fair certainty.

associate with this configuration a certain spectral term and, having found the term empirically, we know the energy of the atom in that

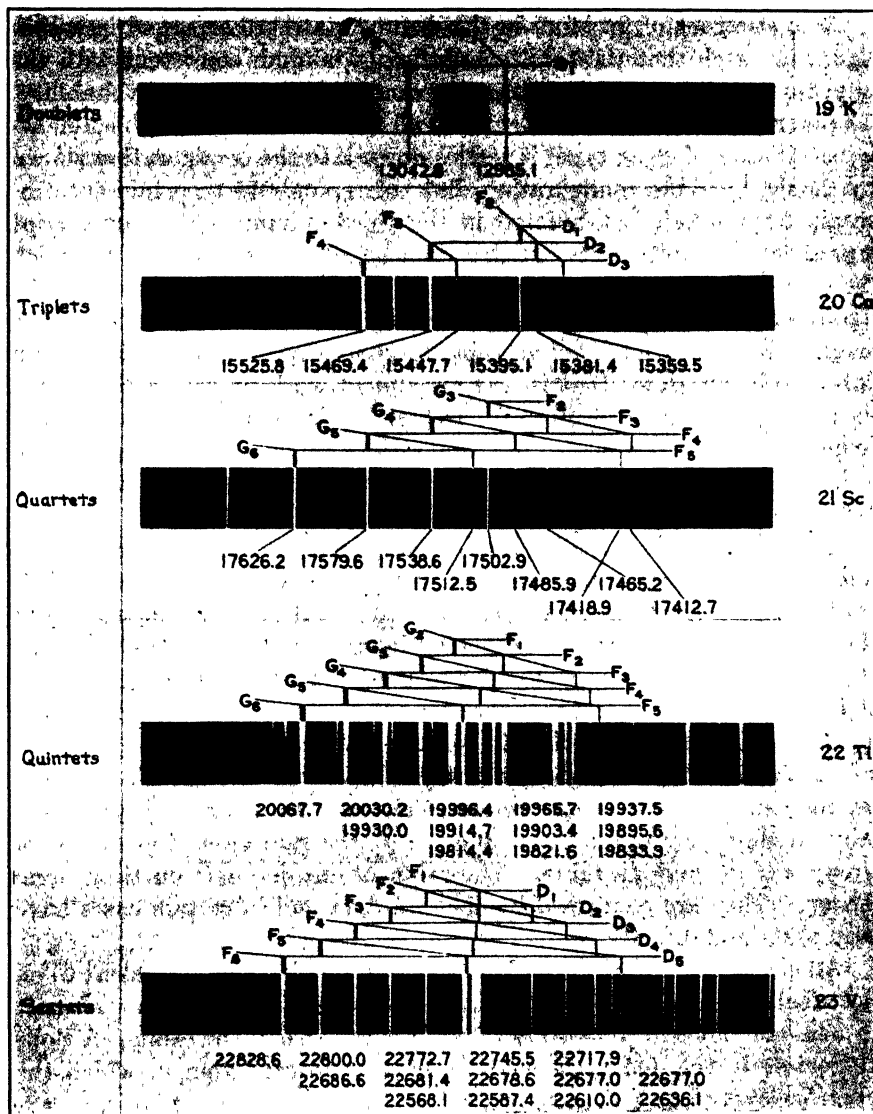


FIG. 1.—EXAMPLES OF VARIOUS TYPES OF SPECTRA OF WHICH THE ANALYSIS FURNISHES THE KEY TO THE SOLUTION OF THE n -BODY PROBLEM OF ATOMIC STRUCTURE. EACH MARKED GROUP REPRESENTS A SINGLE MULTIPLET. FOURTEEN LINES FORM A COMPLETE DF SEXTET. (PHOTOGRAPH BY MEGGERS.)

particular arrangement. The theory enables one to predict directly the type and relative magnitude of many of the terms in spectra which have not yet been classified. For example in certain rare earths where the

lines are so close together that the spectrum, except under high resolving power, appears practically continuous, we shall find systems with the multiplicity twelve.

The electrons of an atom in the normal state are arranged in a configuration such that the total energy is a minimum consistent with the quantum postulates, this being the condition for permanent stability. Therefore, after the atom has emitted all the lines which it is able, following excitation of some type, it settles down into the configuration shown by Table 1. This configuration also corresponds to a certain spectroscopic term which is tabulated in the third column. The superscript represents the multiplicity, singlet, doublet, etc., of the system to which the term belongs and the subscript gives the inner quantum number, the significance and importance of which will appear presently. From the magnitude of this term we are able to compute directly the ionization potential of an atom; that is, the amount of work necessary to remove the most loosely bound electron.¹¹ In fact, by the use of x -ray and spectroscopic data, it is possible to determine the amount of work required to pull any electron from any atom, as far as the data of this nature have been extended.¹²

Each electron in a complicated atom possesses a certain number k of units ($h/2\pi$) of angular momentum. The vector sum of these individual contributions by all the electrons gives the total angular momentum of the atom. This resultant is either an integral or half-integral multiple of the unit $h/2\pi$ and is called j , the inner quantum number. Values of j , corresponding to the configurations shown in Table 1, are indicated by the subscripts to the letters in column 3. Configurations represented by closed or completed groups always have zero angular momentum, the momenta vectors of the separate electrons being directed symmetrically so that they mutually balance, *e. g.*, the rare gases and metals of Group II of the periodic table. The values of j are derived from the general theory. They are confirmed by spectral data and in certain cases have been measured directly.²

An electron revolving in an orbit with the period τ is equivalent to an electrical current e/τ . Such a closed circuit acts as an elementary magnet of magnetic moment $\mu_1 = Ae/\tau$ where A is the area of the orbit. A Bohr magneton is the magnetic moment of a hydrogen atom in which the electron revolves in a circular orbit of radius $5.29 \cdot 10^{-8}$ cm., that is, $n = 1$, $k = 1$. If the magnetic moment of a complicated atom, the vector sum of the magnetic momenta of its planetary electrons, is measured in terms of this Bohr magneton as a unit, and if the classical methods for the addition of vectors are employed, it may be shown that the resultant magnetic moment μ should be numerically equal to the mechanical moment j . This conclusion leads immediately to the normal Zeeman effect in which every spectral line in a magnetic field splits into a normal triplet, a simple

theory of which is readily derivable from classical considerations. Actually, however, we have very few examples of the "normal" Zeeman effect. The atom is not a classical dynamic system and the correct relation between the magnetic and mechanical moments is given by the expression $\mu = gj$ where g is a simple factor such as 2, 1, $\frac{2}{3}$, etc. The g factors are known for most types of spectroscopic terms. For example $g = 2$ for all the S terms of any system.¹³

Hence we are able to determine purely from spectroscopic data the magnetic moment of any atom. The configurations given in Table 1 for

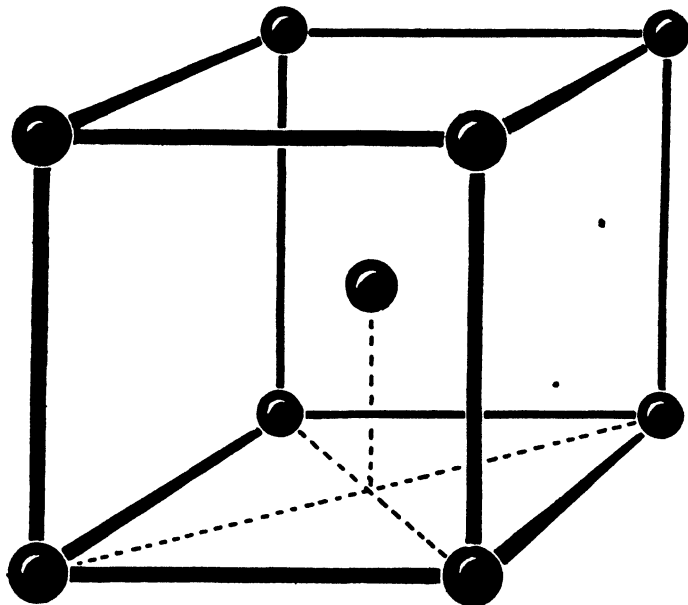


FIG. 2.—SCHEMATIC REPRESENTATION OF THE ELEMENTARY CELL OF A BODY-CENTERED CUBIC. TO OBTAIN PERSPECTIVE IN THIS AND THE FOLLOWING MODELS, VIEW WITH ONE EYE CLOSED.

all the alkalis and Cu, Ag, and Au correspond to an S term with the j value $\frac{1}{2}$. Multiplying this by $g = 2$, we find that the magnetic moment μ of each of these atoms is one Bohr magneton. This has been directly confirmed with a precision of 10 per cent. by the beautiful experiments of Gerlach and Stern¹⁴ who projected atoms of Cu, Ag, and Au with a definite velocity through an inhomogeneous magnetic field and measured their deflection. From the magnitude of the deflection, the geometrical arrangement of the apparatus and the characteristics of the field, the magnetic moment of the atom is readily calculable. No deflection was detected with Zn, Cd, and Hg, and none should be expected since j and hence μ is zero for the electronic configurations characteristic of these atoms, as shown by Table 1. All the elements belonging to Group II, in the vapor state, are therefore diamagnetic; likewise the rare gases for

which j is also zero. Most atoms in the vapor state, however, should be paramagnetic and the exact amount of the paramagnetism is readily predicted by the theoretical considerations outlined.

It would seem that an atomic theory so successful for the vapor state might be extended to the liquid and solid phases. Ultimately, no doubt, this will be the case but at present we are confronted with the very serious difficulty, already mentioned, namely, the distortions of the orbits of the loosely bound electrons by the fields of neighboring atoms. One example is sufficient as an illustration. The single-valence electron of an alkali atom in the vapor state revolves in an elliptical orbit of high eccentricity. The maximum or aphelion distance of the electron may be computed from spectroscopic data. The orbit is constantly precessing so that the effective diameter of the atom is twice this distance. The shortest distance between atoms in the crystal state is known from x -ray crystal analysis or may be computed, assuming a body-centered cubic packing, Fig. 2. We find that in the solid state the atoms are packed so closely that the valence electron does not have sufficient room, as is illustrated by Table 2.

TABLE 2.—*Diameter of Alkali Atoms In A* (10^{-8} Cm.)

	Li	Na	K	Rb	Cs
Shortest distance between atoms (solid)...	3.02	3.71	4.50	4.93	5.31
Diameter of atom (vapor).....	4.75	5.01	6.05	6.32	6.82

All of the ordinary optical orbits of the valence electrons are therefore suppressed in the solid state. This explains in part why a solid piece of metal is unable to emit the arc spectrum characteristic of its vapor. What becomes of the valence electron is at present a matter of conjecture to which we shall refer later. Possibly when the far ultraviolet is made more readily accessible we shall be able to observe line or narrow band radiation from a solid which will furnish definite evidence for its complete structure.

It should be noted that while there is not sufficient room for the free play of the valence electrons in the solid state, there is generally space enough for the underlying shells. These are of much smaller dimensions and they shrink still more with the removal of one or several valence electrons. The theoretical considerations leading to Table 1 were confined to the neutral atom and were based upon arc spectra. However, the theory is equally applicable to ionized atoms. A similar table may be readily prepared for atoms from which one valence electron is removed. Another table may be computed for doubly charged atoms, that is atoms which have lost two electrons, and so on. In fact the theory of atomic structure becomes simpler and more uniquely consistent for the higher

stages of ionization. Ionized atoms emit different types of spectra, the character of all of which may be predicted. In many cases these so-called spark spectra have been fairly completely observed and properly correlated in series by the spectroscopist. Spectra of very highly ionized atoms are produced with difficulty. Millikan and Bowen¹⁵ have succeeded in exciting a few lines in the chlorine atom from which six electrons have been removed, and in numerous atoms which have been three and four-fold ionized. The spectra of singly and doubly ionized atoms are quite readily observed in ordinary spark discharges.

MAGNETIC PROPERTIES OF SOLUTIONS

In an aqueous solution of a salt the metal atom occurs as a positively charged ion. The rare-earth atom in solution is usually triply ionized and in a few cases quadruply ionized, having lost three or four valence electrons, respectively. Under such circumstances the atoms are of sufficiently small dimensions that they may be crowded in between the water molecules and other atoms without destroying the essential features of their ionic structure characteristic of the vapor state. Solutions of the rare-earth salts are strongly paramagnetic. The susceptibility, which is a measure of the paramagnetism, has been experimentally determined and values in terms of the Weiss magneton have been found for each of the rare-earth ions. The number of Weiss magnetons may be obtained theoretically by multiplying the number of Bohr magnetons by $4.97\sqrt{(j+1)/j}$. The number of Bohr magnetons follows directly from the values of j and g corresponding to the spectroscopic term representing the normal state of the vapor ion. While the spark spectra of the triply ionized rare earths have not been experimentally investigated, the general theory of spectroscopy¹⁶ permits their evaluation as given in Table 3.

TABLE 3.—*Magneton Numbers for the Rare Earths (Hund¹⁶)*

Element	Spectral Term	j	g	Bohr Magnetons $\mu = jg$	Computed Weiss Magnetons	Observed Weiss Magnetons	
						Cabrera ¹⁷	St. Meyer ¹⁸
La ⁺⁺⁺	¹ S	0		0.00	0		{ La ⁺⁺⁺ diamagnetic Ce ⁺⁺⁺⁺ 0.8 13.8 (Pr ⁺⁺)
Ce ⁺⁺⁺	² F	$\frac{5}{2}$	$\frac{3}{2}$	2.14	12.5	11.4	
Pr ⁺⁺⁺	² H	4	$\frac{5}{2}$	3.20	17.8	17.8	17.3
Nd ⁺⁺⁺	⁴ J	$\frac{9}{2}$	$\frac{5}{2}$	3.27	17.8	18.0	17.5
P ⁺⁺⁺	² J	4	$\frac{3}{2}$	2.40	13.4		
Sm ⁺⁺⁺	² H	$\frac{5}{2}$	$\frac{3}{2}$	0.71	4.2	8.0	7.0
Eu ⁺⁺⁺	² F	0		0.00	0.0	17.9	18.0
Gd ⁺⁺⁺	² S	$\frac{7}{2}$	2	7.00	39.4	40.0	40.2
Tb ⁺⁺⁺	² F	6	$\frac{5}{2}$	9.00	48.3	47.1	44.8
Dy ⁺⁺⁺	² H	$\frac{15}{2}$	$\frac{5}{2}$	10.00	52.8	52.2	53.0
Ho ⁺⁺⁺	² J	8	$\frac{5}{2}$	10.00	52.8	52.0	51.9
Er ⁺⁺⁺	² J	$\frac{15}{2}$	$\frac{5}{2}$	9.00	47.7	47.0	46.7
Tm ⁺⁺⁺	² H	6	$\frac{5}{2}$	7.00	37.6	35.6	37.5
Yb ⁺⁺⁺	² F	$\frac{7}{2}$	$\frac{3}{2}$	4.00	22.5	21.9	22.5
Lu ⁺⁺⁺	¹ S	0		0.00	0.0		diamagnetic

The sixth column gives the number of Weiss magnetons as computed solely from spectroscopic theory. The last two columns contain the direct magnetic measurements. The agreement is better illustrated by Fig. 3. The only point which deviates seriously from the theoretical curve is for Eu which v. Hevesy has shown always contains Gd as an impurity, up to 20 per cent.

The correct prediction of magnetic properties of solutions from spectroscopic theory for the vapor state is an achievement of which the importance cannot be overestimated. This is an excellent illustration suggestive of a means whereby our knowledge of atomic structure may be extended to the solid state. While undoubtedly the actual binding

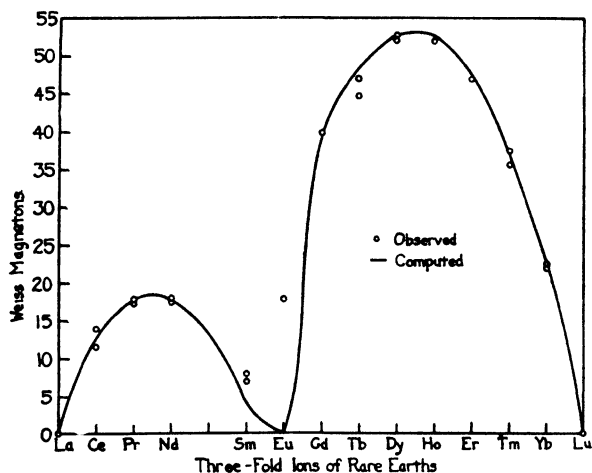


FIG. 3.—OBSERVED MAGNETON NUMBERS OF THE RARE-EARTH IONS AND VALUES COMPUTED FROM SPECTROSCOPIC THEORY.

forces on the outer electrons of the ion are somewhat different in the solution from those in the vapor phase, a point which may be investigated by direct experiment when the soft x -ray and ultraviolet technique is more thoroughly developed, yet the quantum numbers and their relation to magnetic moment appear unaltered in the process of change of state.

If these ideas are extended to the ions of the much lighter paramagnetic elements from Ca^{++} to Zn^{++} , embracing the iron group, the experimental and theoretical data appear in fair qualitative agreement, but by no means so good as that illustrated by the rare earths. We shall not go into the details of this matter, which are somewhat involved. The basic spectroscopic term in Mn^{++} is ${}^6\text{S}_{5/2}$ which leads to the value 29.4 Weiss magnetons. Observed data¹⁹ range from 29 to 29.3. The same spectral term applies also to Fe^{+++} ; the observed value of the magnetic moment is 29 Weiss magnetons.

CRYSTAL FORMATION

We shall now consider the nature of the forces which lead to crystallization. A rare gas atom represents an extremely stable, closed configuration of electronic orbits having the resultant angular and magnetic momentum zero, as indicated in Table 1. There is considerable evidence, some of which will be apparent later, that the atomic structure of the gas is preserved in the frozen or crystalline state. Undoubtedly the binding energies of the various electrons are altered by the presence of closely neighboring atoms but the general configuration and quantum numbers descriptive of the orbits are probably retained in the solid. Fortunately,

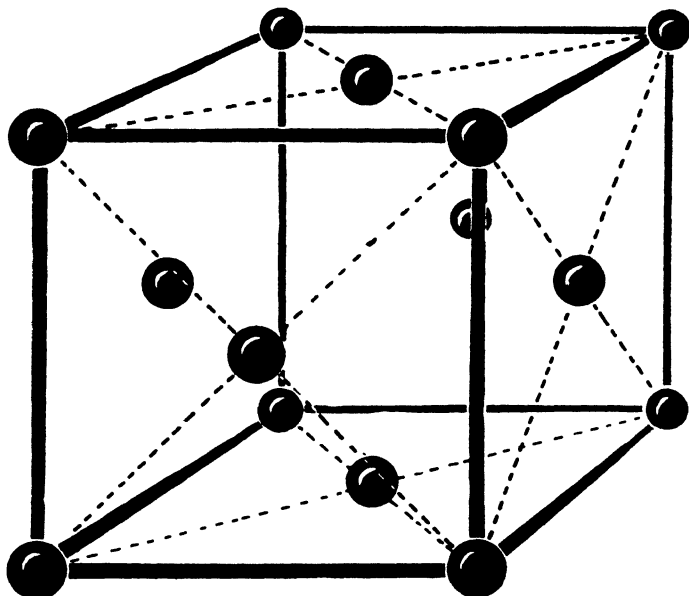


FIG. 4.—SCHEMATIC REPRESENTATION OF THE ELEMENTARY CELL OF A FACE-CENTERED CUBIC.

unlike the metals, there appears to be sufficient room for these orbits. Argon crystallizes in the face-centered cubic system, Fig. 4, with the lattice space 3.84 Å. The isolated atom certainly has a smaller diameter. The forces exerted between two neutral argon atoms, on account of their symmetrical configuration, must decrease with a very high power of their distance apart. While the inverse square law may hold at all distances for the action of an element of charge in one atom on an element of charge in another atom, the integrated effect of all elements expressed in terms of the single distance r between the centers or nuclei of the atoms is in general a complicated power series in r^{-n} where certain terms with a large exponent are effective, especially when the distance between centers becomes comparable to the atomic dimensions.

Let us assume, therefore, that there exists an attractive force between the argon atoms which may be represented roughly as proportional to r^{-n} . If only this force were present the atoms would be continually attracted and would eventually coalesce. To counteract such a tendency there must exist simultaneously a repulsive force which may be represented as proportional to r^{-m} . In other words, merely as a convenient approximation, we retain in the power series development only two important terms having opposite signs.

In so far, therefore, as this approximation is justifiable, and we shall find it in general sufficient, one should be able to evaluate these terms in the force equation, empirically from data on gaseous argon and extend them to the crystal state. In the crystal the distances between atoms must be such that an equilibrium position is attained in which the repulsive and attractive forces counterbalance and for which the potential energy of the configuration has a minimum value.

The viscosity of a gas may be theoretically expressed as a complicated function involving the dynamics of a collision between two atoms. This obviously depends upon the law of force. Also the van der Waals equation, which shows the departures of the pv relation from Boyle's law at high pressure, may be interpreted in terms of the forces exerted between two atoms. Thermal conductivity of a gas likewise involves the mechanism of atomic collision. Using experimental data of the above character obtained directly from the behavior of the gas, Lennard-Jones²⁰ has investigated the nature and magnitude of the repulsive and attractive forces. He finds that in argon these forces require a crystal having the face-centered cubic lattice as actually observed, even though the interatomic distance for such a lattice be greater than that for a simple cubic. The predicted lattice space was 3.89 Å; the observed value is 3.84 Å.

POLAR COMPOUNDS—ALKALI-HALIDE CRYSTALS

Both physical and chemical evidence have shown that the halogen gases, in the neutral atomic state, possess a strong affinity for an electron, tending to attract an extra electron into its planetary configuration, thus becoming a singly charged negative ion. Referring to Table 1, it is apparent that the addition of one electron to a halogen atom produces an outer closed structure identical with that of the succeeding rare gas. It is now possible to evaluate quantitatively the magnitude of this electron affinity by the ingenious method of v. Angerer and Müller,²¹ who have determined the photoelectric absorption of an alkali-halide vapor which at high temperature is dissociated into negative halide ions and positive alkali ions.

The alkali-halide crystal is a configuration consisting of these negative halide ions and positive alkali ions generally arranged in a regular cubic

system as illustrated in Fig. 5. A closer representation of the actual packing is shown in Fig. 6 for NaBr where the various electronic orbits are schematically indicated. The valence electron of each sodium atom has been literally squeezed off into a bromine atom by the close packing. X-ray crystal analysis merely shows the geometrical form of the lattice structure; it does not distinguish between an atomic latticelike argon and the assumed ionic lattice.* Some evidence for the latter is obtained spectroscopically from an investigation of the residual rays or metallic

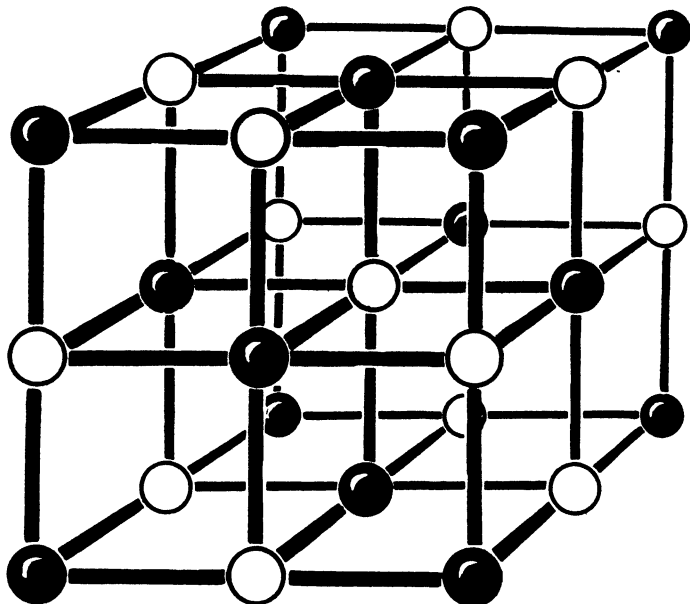


FIG. 5.—SCHEMATIC REPRESENTATION OF THE ELEMENTARY CELL OF A REGULAR CUBIC. NOTE THAT THE BLACK SPHERES ALONE FORM THE ELEMENTARY CELL OF A FACE-CENTERED CUBIC.

reflection of the salt in the infrared.²² A satisfactory proof, however, of the ionic character is found in the following discussion.

The K^+ ion and the Cl^- ion resemble argon except for a small difference in size (K^+ is slightly smaller and Cl^- larger²³). Hence it should be possible to extend the data on argon to the KCl crystal, consideration being given to the additional Coulomb or inverse square forces arising from the alternative arrangement of positive and negative ions. Similar data on neon should be applicable to the crystal NaF. Spectroscopic evidence again shows that the calcium atom, with its two valence electrons removed, and the sulfur atom which, by virtue of its electron affinity, has captured two electrons, have an electronic structure identical, except for size, with that of argon. That is Ca^{++} , A and S^{--} , and for the

* See qualifying statement later.

same reason Mg^{++} , Ne, and O^{--} are similar. Hence data on the rare gases A and Ne should lead to predictions relative to the crystal structure of CaS and MgO which form a rock-salt type of crystal. Table 4 gives the lattice space δ_0 , the distance between two ions of the same type, as observed and as computed by Lennard-Jones²⁰ from rare gas data. All these values have been decreased by about 1 per cent. to apply at 0°

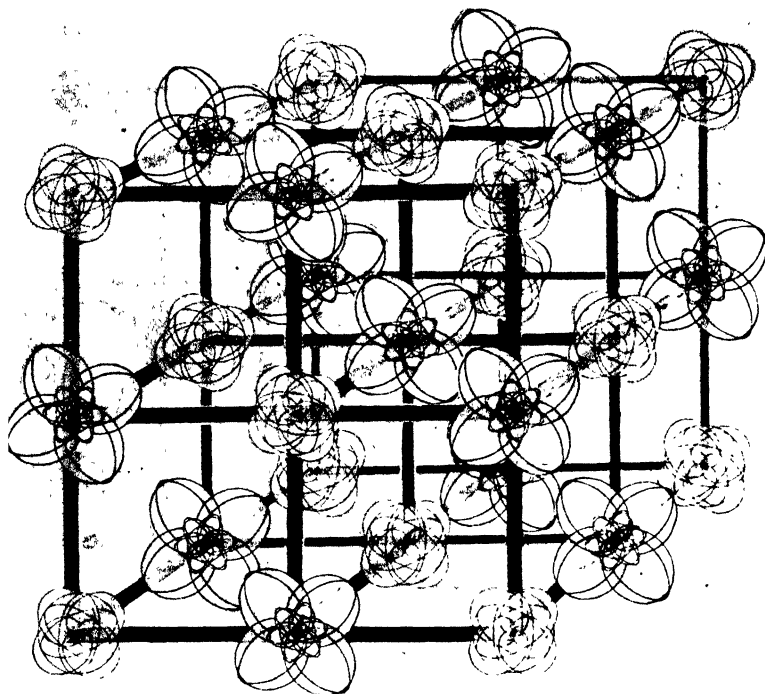


FIG. 6.—THE SPECTROSCOPIST'S CONCEPTION OF A NaBr CRYSTAL BELONGING TO THE REGULAR CUBIC SYSTEM. THE ELLIPSES REPRESENT ELECTRON ORBITS CHARACTERISTIC OF THE VARIOUS ATOMS. THE Na^+ IONS ARE SOMEWHAT SMALLER THAN THE Br^- IONS.

absolute for reasons which will presently appear. The correction factor is obtained from the linear coefficient of expansion.

TABLE 4.—*Lattice Spacing, Observed and Computed from Data on Rare Gas*

Crystal	Observed	Computed
KCl.....	6.19 A	6.16 A
CaS.....	5.63	5.58
NaF.....	4.57	4.54
MgO.....	4.14	4.22

When the law of force between any pair of ions in a crystal is known it is merely a somewhat tedious problem of geometry to compute the potential energy of the crystal. This involves e^2 , the lattice space δ and certain constants which depend upon the crystal system. For example the coulomb force contributes the amount $-a/\delta$, where $a = 13.94 e^2$, to the potential energy φ of a single elementary cell of the NaCl type as illustrated in Fig. 5. In addition we have the contribution made by the complicated attractive and repulsive forces characteristic of a rare-gas crystal. We shall as an approximation group these together as a single term and represent the total energy of a single cell in the crystal by Eq. (1):

$$\varphi = -\frac{a}{\delta} + be^{-c\delta} \quad (1)$$

where the only empirical constant is $c = 1.725 \cdot 10^8$. The constant b is expressible in terms of a , c , and the grating space, and so may be eliminated.*

If we compress a crystal, work must be done against the electrostatic forces. All the ions are crowded more closely together, that is, δ in Eq. (1) decreases. To simplify the conditions we shall assume the experiments are carried out at 0° absolute; hence, we do not need to consider terms which otherwise contribute to the kinetic energy of the atoms and specific heat. All the work of compression is utilized in increasing the potential energy, and we have the general thermodynamic relation²⁴

$$\frac{d\varphi}{d\delta} + 3p\delta^2 = 0 \quad (2)$$

where p is the applied pressure. Compressibility is defined by the formula

$$\kappa = \frac{1}{\delta_0^3} \frac{d\delta^3}{dp} \quad (3)$$

where δ_0 is the lattice space at zero pressure (or one atmosphere since very high pressures are required to produce an appreciable alteration in δ). From Eqs. (1), (2) and (3) one obtains for the compressibility κ_0 at $p = 0$ the following expression:

$$\kappa_0 = \frac{9\delta_0^3}{a\left(\frac{2}{\delta_0} - c\right)} \quad (4)$$

It may be further shown that the pressure coefficient of compressibility ψ_0 is expressed by Eq. (5).

$$\psi_0 = \frac{1}{\kappa_0} \left(\frac{\delta\kappa}{\delta p} \right)_T = \kappa_0^2 \frac{a(6 - c^2\delta_0^2)}{27\delta_0^4} + 2\kappa_0 \quad (5)$$

* Many different functions have been proposed for the second term. Some of these are discussed by Born²² who is responsible for the general theory and applications of lattice energy computations. Slater²⁴ uses a Taylor series expansion and is able to evaluate the electronic charge from compressibility data, obtaining $5.1 \cdot 10^{-10}$ e. s. u. in good agreement with Millikan's value $4.774 \cdot 10^{-10}$.

The fourth column of Table 5 lists Slater's measurements²⁴ of the compressibilities for several halides having the lattice spacing shown in column 2. The third column gives the values computed by Eq. (4). The observed and computed data are in excellent agreement. The fifth column gives the pressure coefficients of compressibility computed by Eq. (5) using computed values of κ_0 , and the sixth column, Slater's measurements. The agreement is qualitatively good. This is therefore an example where the theory of atomic structure extended to crystal formation leads to a more satisfactory understanding of certain phenomena of an engineering character.

TABLE 5.—*Lattice Energies, Compressibilities and Pressure Coefficients of Compressibility of the Alkali Halides*

Crystal	$\delta_0 \cdot 10^8$ cm.	$\kappa_0 \cdot 10^{12}$		$-\psi_0 \cdot 10^{12}$		U in Kg Cal/Mol		
		Com- puted	Ob- served	Com- puted	Ob- served	Com- puted	Ob- served	Slater
LiF.....	3 94	1.4	1.4	6	12	250	254	231
LiCl.....	5 08	2 8	2 7	15	20	200	205	189
LiBr.....	5.43	3.3	3.2	19	24	189	191	180
NaCl.....	5 55	3 6	3 3	20	22	186	181	178
NaBr.....	5 85	4.1	3 9	24	25	177	169	169
KF.....	5.28	3 1	3 2	17	20	194	196	182
KCl.....	6 19	4 8	4.8	29	27	168	165	164
KBr.....	6.47	5 4	5.5	34	32	162	154	157
KI.....	6 96	6 7	7 0	44	39	151	143	148
RbBr.....	6 74	6.1	6 5	39	35	156	150	152
RbI.....	7.20	7 3	7 6	49	43	147	139	147

By use of Eq. (1) we may compute the total potential energy of the elementary cell or the work $U = -\varphi$ necessary to completely vaporize it, that is, to remove the various ions to infinity. Instead of expressing the quantity in ergs per unit cell we shall use the more customary chemical notation, kg cal per gram mol. There are $6.060 \cdot 10^{23}$ molecules in a mol and four molecules per cell in the simple cubic crystal. Using these data and the mechanical equivalent of heat, Eq. (1) may be expressed as follows:

$$U = 1.150 \cdot 10^{-5} \frac{1}{\delta_0} \left(1 - \frac{1}{c\delta_0} \right) \text{ kg cal/mol} \quad (6)$$

Values computed in this manner are tabulated in the seventh column of Table 5. It is of interest that while the equilibrium of the crystal depends on the mutual balancing of the ordinary Coulomb force and the special forces arising from the finite size of the ions, the energy of the configuration arises mainly in the Coulomb field. The exponential term in Eq. (1) is merely of a corrective nature, being always less than 10 per cent. of the first term.

The work required to destroy the crystal has not been measured directly but it may be obtained through an ingenious cyclic process, first employed by Born, involving thermochemical and atomic constants. Starting with a gram mol of sodium chloride crystal, for example, we do the work Q_{NaCl} , the heat of formation as measured by the chemist, and obtain a gram atom of solid sodium and one-half gram mol of chlorine gas. The solid sodium is then sublimed requiring the work S_{Na} , the latent heat of sublimation. The diatomic chlorine is converted to monatomic chlorine by the work D_{Cl} representing the heat of dissociation. We now have a gram atom of sodium vapor and a gram atom of monatomic chlorine gas. Every sodium atom is then ionized by removing the valence electron thus doing the work J_{Na} . We obtain $6.060 \cdot 10^{23}$ electrons which are allowed to unite with the corresponding number of chlorine atoms. In this process the work E_{Cl} is done by the system. The final product is a gram atom of negative chlorine atoms. By definition, therefore, the total work expended is equal to U as follows:

$$U = Q_{\text{NaCl}} + S_{\text{Na}} + J_{\text{Na}} + D_{\text{Cl}} - E_{\text{Cl}} \quad (7)$$

All of these quantities are known from direct experiment. In the eighth column of Table 5 are listed the experimental values of U obtained in this manner as summarized in an extensive paper by Grimm and Herzfeld.²⁵ In the last column are Slater's estimates which were derived from compressibility data by a procedure considerably different from that described above.

It is possible to evaluate U the work required to destroy a KCl crystal through the consideration solely of physical data on the rare gas argon. Thus Lennard-Jones' empirically derived force function for argon leads to $U = 179$ kg cal/mol for KCl and the data on neon predict $U = 239$ kg cal/mol for NaF. Furthermore the argon data indicate a compressibility for KCl of $\kappa_0 = 3 \cdot 10^{-12}$ which is in qualitative agreement with experiment.

LATTICE STRUCTURE OF METALS

Lattice energy and compressibility computations of the type described have been extended with success to other forms of crystal, such as the ZnS and CaF_2 structures where the positive metal ion carries a double charge. The calcium atoms in CaF_2 , Fig. 7, form a face-centered cube. This is precisely the structure of metallic calcium. Since there is not sufficient room in the calcium crystal for the free play of both valence electrons, it appears logical to assume that these might replace the spaces occupied by the fluorine atoms in CaF_2 . Hence Ca, and presumably Ba and Sr, metal crystals might be expected to form a CaF_2 type of lattice structure made up of doubly charged metal ions and electrons. There is also the possibility of another arrangement consisting of singly charged calcium atoms and electrons in a regular cubic formation like NaCl. The

metals Cu, Ag, and Au also crystallize in the face-centered cubic system so that a lattice of the NaCl type with Cu^+ and electrons is geometrically possible.

A great deal of effort has been expended in attempts to establish a satisfactory theory of ionic lattice structure in metal crystals by extending the general conceptions employed above in the consideration of polar crystal formation.^{26,28} While these developments have not been crowned with success, there are enough qualitative agreements between the theoretical and observed data to involve a serious consideration as to

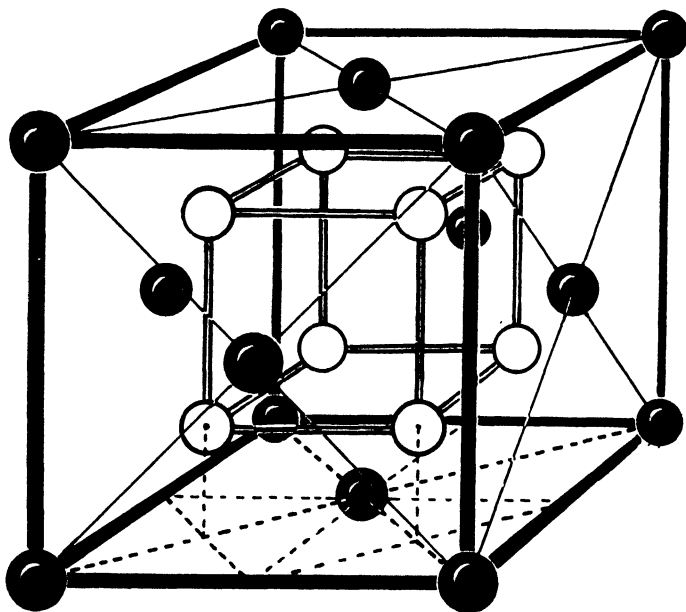


FIG. 7.—SCHEMATIC REPRESENTATION OF THE ELEMENTARY CELL OF THE CaF_2 CRYSTAL.

whether they may be merely numerical coincidences. Arguments of a thermodynamic nature,²⁷ which have been advanced against the theory, appear faulty; in fact, the same reasoning is applicable to the structure of a crystal such as NaCl. On the other hand the alkali metals which crystallize in the body-centered cubic system present a puzzle. There is no way by which alkali ions and electrons may be geometrically arranged with a symmetrical elementary cell conforming to the observed structure of the metal, and yet the assumption of an ion-electron lattice yields certain correct numerical relationships. Thomson²⁸ has proposed a larger unit cell which partially overcomes this objection but which appears rather artificial.

The work U required to destroy a gram mol of metal crystal consisting of singly charged metal ions and electrons, at 0° absolute, that is, the work

necessary for the removal to infinity of all the ions and electrons is given by the relation

$$U_1 = J_1 + S \quad (8)$$

where S is the heat of sublimation and J_1 the work required to ionize $6.060 \cdot 10^{23}$ metal vapor atoms, *i. e.*, the ionization potential for the neutral atom referred to a gram atom. If the metal ion occurs in the crystal doubly charged we have

$$U_2 = J_1 + J_2 + S \quad (9)$$

where J_2 represents the work necessary to remove the second valence electron from the atom after the first has been removed, *i. e.*, the second ionization potential. The quantities on the right-hand side of Eqs. (8) and (9) are, in general, known from spectroscopic, critical potential and thermochemical data. Table 6 gives the lattice space, corrected for 0° absolute, as measured by x -ray data or density determinations, for several elements belonging to the face-centered cubical system. This is also the side of the unit cell of the regular cubic which is geometrically possible for the alternate arrangement of singly charged ions and electrons. The fifth column gives the value of the lattice energy U determined through the use of Eq. (8).

TABLE 6.—*Ion-electron Lattice of NaCl Type*

Metal	a_0	J_1	S	U Kg Cal/Mol		$-x_0 \cdot 10^{12}$	
				Observed	Computed	Observed ¹¹	Computed
Cu.....	3.59 <i>A</i>	177.4	75	252	269	.66	1.1
Ag.....	4.06	174.0	65	239	243	.90	1.5
Au.....	4.05	212.2	84	296	243	.53	1.5
Ca.....	5.52	140.4	38	178	186	4.8	3.5
Sr.....	6.04	130.8	38	169	172	7.8	4.4
Ba.....	6.15	119.7	37	157	169		4.7

The work U may be computed by Eq. (6) if we assume that the forces existing in an ion-electron lattice are identical to those in an ion-ion lattice. As an approximation for U this may be sufficient since, as pointed out earlier, the main contribution to the energy arises in the Coulomb forces. The sixth column of Table 6, therefore, shows the energy values computed with the same constants employed for the alkali-halides. The agreement between the computed and observed data is, except for Au, almost within the accuracy with which the heats of sublimation are known. The observed compressibility and that computed by Eq. (4) show agreement merely in order of magnitude. The theoretical values of U for Ca, Sr and Ba appear somewhat less consistent when a CaF_2 type of ion-electron crystal is assumed.

It is possibly more logical to employ some *a priori* reasonable function containing a single empirical constant for the energy of the unit cell of a particular metal crystal and evaluate this constant by use of the compressibility coefficient κ_0 . The astonishing and important feature of the lattice theory as applied to the alkali-halogen crystals was that a single empirical constant in a simple function sufficed for all the salts. When this procedure is extended to metals we find a different constant for each metal of the same assumed crystal structure. However it is of interest to see whether the compressibility data are consistent with the observed lattice energies. We shall try two different relations for the energy; Eq. (1), which was so successful for the halides, and Eq. (10) which has been more generally employed by Born,²² Fajans, Weigle and many others:

$$\varphi = -\frac{a}{\delta} + be^{-c\delta} \quad (1)$$

$$\varphi = -\frac{a}{\delta} + \frac{b}{\delta^n} \quad (10)$$

where $a = 13.94e^2$ for the NaCl structure and $a = 46.93e^2$ for the CaF_2 structure. The single empirical constant in each of these equations is c and n , respectively, since the constant b may be expressed in terms of a and c or a and n . The results for five metals are summarized in Table 7.

TABLE 7.—*Ion-electron Lattices*

Metal	$-\kappa_0 \cdot 10^{12}$ Bridgman ²³	NaCl Type of Crystal					
		By Eq. (1)		By Eq. (10)		$U = J_1 + \sum S$ (obs.)	
		c	U	n	U		
Cu.....	.66	$2.55 \cdot 10^8$	287	8.1	282	252	
Ag.....	.90	2.60	257	9.5	254	239	
Au.....	.53	4.04	262	15.4	267	296	
Ca.....	4.8	1.36	180	6.5	177	178	
Sr.....	7.8	1.13	162	5.8	158	169	
		CaF ₂ Type of Crystal				$U = J_1 + J_2 + S$	J_2
Ca.....	4.8	$6.57 \cdot 10^7$	578	2.6	437	451	272.6
Sr.....	7.8	5.68	482	2.4	379	422	253.3

The agreement between computed and observed values of U for Ca and Sr argues for an NaCl structure in which the ions carry a single charge. However, especially with Cu, Ag and Au, discrepancies by either formula occur which cannot be attributed to an error in the heat of sublimation S . It is doubtful if so large an error could have been introduced in converting Bridgman's compressibilities to 0° abs. Admitting the general hypothesis, the basic trouble would appear to be in the

empirically selected formulas (1) and (10). Evidently these are far too simple relations for ion-electron lattices. A general expression must be able to account for the fact that Ag and Au, with almost exactly the same grating space, have compressibilities in the ratio 9:5 and lattice energies in the ratio 4:5. Bridgman²⁹ has considered the subject in some detail but so far without definite conclusions as to the actual existence of the ion-electron lattices.

PHOTOELECTRIC AND OTHER PHENOMENA

If metal crystals represent an ion-electron lattice there should be some relation between the characteristics of the lattice and the photoelectric or thermionic properties of the metal. By means of some rather questionable assumptions Weigle³⁰ has computed the thermionic work function of the alkalis in terms of the lattice energy $= J + S$, thereby obtaining excellent agreement with experiment. Possibly a more logical procedure, however, is that adopted in his second paper³¹ on calcium in which the potential is computed at the point occupied by a given ion or electron due to all the other ions and electrons. Dr. Ruark and the writer have made a calculation, similar in principle, for the NaCl lattice, following the general mathematical procedure of Madelung.³² We shall consider the lattice as made up of point charges so that only the inverse square law of force is effective. The work required to remove either a single positive or negative ion is equal to the computed potential times the electronic charge, provided we neglect the distortion of the crystal at the surface and that arising in the removal of an elementary charge. This work depends only slightly upon the depth from which the charge is removed, as follows:

Removal of electron or ion from crystal surface (plane 0) $= 3.364e^2/\delta_0$
 ergs $\approx 4.82 \cdot 10^{-7}/\delta_0$ volts.

Removal of electron or ion from plane 1 $= 3.498e^2/\delta_0$ ergs
 $\approx 5.00 \cdot 10^{-7} \cdot / \delta_0$ volts.

Removal of electron or ion from planes 2, 3, etc. $= 3.497e^2/\delta_0$ ergs
 $\approx 5.00 \cdot 10^{-7}/\delta_0$ volts.

Hence for copper, for which $\delta_0 = 3.59 \cdot 10^{-8}$ cm., we find that the work required to remove either an ion or an electron from an underlying layer in the simple cubic lattice corresponds to 13.9 volts, while the photoelectric threshold is only 4.1 volts. However, on the basis of any theory of the structure of metals, it is not always necessary that the photoelectron be the original valence electron as is ordinarily assumed. In this particular case for example it requires much less work to remove an electron from the copper ion than to remove either the ion itself or the valence electron forming the lattice. Let us consider the following cyclic process. We shall first pull out the Cu^+ ion requiring 13.9 volts then ionize the vapor ion by removing its most loosely bound electron. The

transition $\text{Cu}^+ \rightarrow \text{Cu}^{++}$ requires 21 volts as estimated by Grimm and Herzfeld²⁵ from thermochemical data. As an independent process, we shall photoelectrically eject the same electron from the Cu^+ ion in the crystal requiring the work L and then remove the Cu^{++} ion from the crystal by the expenditure of the work $2 \cdot 13.9 = 27.8$ volts. The final result is the same in either case so that $13.9 + 21 = L + 27.8$ or L , the computed photoelectric threshold, is 7.1 volts, considerably less than the work required to eject the valence electron from the crystal but still larger than the experimental value. These computations might be refined by correcting for the size of the ions, assumed as point charges and for the distortion of the surface and interior of the crystal, but the outlook is not very promising in view of the mathematical complexity.

Confirmatory evidence sometimes advanced for the ionic character of the halogen-alkali salts is presented by the type of diffraction pattern obtained, for example, in the Debye-Sherrer or Hull powder analysis method. Thus while in KI or KBr the alkali atoms and the halogen atoms lie on two interlocked face-centered cubes with the formation of a simple cubic, the diffracting powers of the two atoms differ so much that the observed pattern is characteristic of a face-centered cubic system. On the other hand the diffracting powers of the two types of atom in KCl are so nearly identical that even with greatly prolonged exposure no lines due to incomplete interference are observable; the pattern is strictly that of a simple cubic.³³ From this the inference may be drawn that in the KCl crystal each atom possesses the same number of electrons, 18, and hence occurs as an ion. In this conclusion we neglect consideration of the fact that the electrons are more closely bound in K^+ than in Cl^- and hence might scatter differently.

A similar type of argument has been proposed against the ion-electron lattice structure of metals.³⁴ In the diffraction pattern of lithium no evidence is found for an electron lattice, whereas there are available for scattering only twice as many electrons in the lithium ions as in the rest of the structure. It should be emphasized, however, that the interpretation of experiments on x-ray scattering as related to electron grouping is at present highly speculative.³⁵

Possibly the ion-electron lattice idea may be preserved by considering the electrons in rapid oscillation about their equilibrium positions. Under such conditions, as with a rigid lattice, they would not contribute angular momentum to the structure. Many properties of the metal, therefore, should be characteristic of the ions and might be predicted from spectroscopic data, as has been illustrated by the magnetic behavior of the rare-earth ions in aqueous solution. For example, were this conception correct, all the solid metals of Group I should be diamagnetic and those of Group II either diamagnetic or showing paramagnetism amounting to 7 Weiss magnetons depending upon their ionic structure.

Cu, Ag and Au are definitely diamagnetic but certain of the alkalis appear to be paramagnetic.

It may be shown from classical electrodynamics that if a magnetized iron needle or cylinder is suddenly demagnetized, the loss of magnetic moment should produce a mechanical moment on the system resulting in a slight tendency for the needle to spin about its axis (Einstein-deHaas effect³⁶). Conversely, the spinning of an iron rod about its axis produces a magnetic moment (Barnett effect³⁷). Extensive experiments, developed from these two opposite points of view, have proved that the ratio of magnetic to mechanical moment is exactly two, *i. e.*, $\mu = gj$; where $g = 2$. If we may apply spectroscopic reasoning³⁸ to solid iron we may conclude that each iron atom is in an *S* state since the *S* terms have a g value of 2. Hund's theory⁷ shows that the only *normal S* term for iron occurs in the three-fold ion Fe^{+++} for which the basic level is 6S . All the magneto-mechanical effects observed in iron, therefore, could be interpreted if we assume that the body-centered cubic structure of iron represented a lattice of the three-fold ions. Curiously enough this is the only structure which, from a purely geometrical standpoint, will satisfactorily take care of the remaining electrons. The lattice is geometrically complete if the equilibrium positions of the electrons occur at the center of each edge and each face of the elementary cube. In a somewhat similar manner the magneto-mechanical properties of cobalt and nickel may be correlated.

CONCLUSION

It must be admitted that up to the present moment the theory of atomic structure has contributed little of a definite nature to our knowledge of the solid state.³⁹ We have confined ourselves to a very superficial consideration of but two general types of phenomena, paramagnetism and crystal structure, hoping that some opening would appear for the powerful entering wedge of spectroscopy. The consideration of the vast accumulation of data on thermal and electrical conductivity, specific heats, thermoelectric and many other physical phenomena does not appear capable of yielding immediate results of a more definite character.

One source of trouble lies in the paucity of experimental data in almost every channel along which the theoretical developments have seemed promising. We should have information concerning the works of ionization from the outer levels of atoms in metallic and salt crystals, that is, measurements of the softest x -ray limits. Many of these absorption limits are within reach of the vacuum grating and fluorite spectrograph and might be located by direct determination of relative absorption or reflection coefficients. Further data are desirable on refractive indices or solids and solutions, especially in the ultraviolet and across absorption bands. The woeful deficiency of experimental material is well illustrated in the subject of molecular refraction and ionic deformability, a field

which offers great promise for extending the conceptions of spectroscopy to the solid state.⁴⁰ Thus from data on line emission of the vapor one may compute the molecular refraction of the various ions forming a salt and from this predict the location of the ultraviolet absorption bands effective in dispersion. These bands for all of the alkali halides lie between 600 and 2000 Å. Not a single experimental measurement has ever been made either in absorption or refraction on these materials in this spectral range.

It is important that x-ray scattering experiments be developed at least to a stage where one may definitely conclude whether or not an atom exists as an ion in the metal. The observations on the photoelectric limit of metals are hopelessly discordant and almost no reliable data for the magneton numbers of the solid elements are available.

Possibly the most easily secured immediate results could be obtained from a systematic investigation of the absorption of aqueous solutions of ionized salts especially to the limit of the fluorite spectrograph. In an aqueous solution of KI, for example, the absorption by the potassium ions should lie in the far ultraviolet but that due to the iodine ions should be readily observable. All the halogen⁴¹ salts in solution show a sharp absorption band in the near ultraviolet with the indication of another band closer to the limit of the quartz spectrograph. My colleague, Dr. W. R. Brode, finds that the first band is probably due to absorption by a trace of free halogen modified by the presence of the water. The band of higher frequency is undoubtedly related to the absorption by the most loosely bound electrons in the halogen ion, and to the absorption of the gaseous ion.²¹ Investigation of the shift of such bands in the salt vapor, in aqueous solution and in the salt crystal is of great importance.

The only serious difficulty in extending the conceptions of spectroscopy to the determination of energy levels of the atom in the liquid and solid states lies in the astonishingly large variation of the "softest" absorption limits with the temperature. It is not clear why an absorption band or the sensitivity band for photoelectric conduction⁴² may shift toward the ultraviolet by an amount corresponding to nearly a volt on lowering the temperature to a few degrees absolute.

In spite of the difficulties enumerated one should recall that the development of the modern theory of atomic structure and spectroscopy has extended over a period of less than 15 years. The advances made in spectroscopy during the past two years have exceeded those in all preceding history. Our present knowledge of the solid state corresponds in many respects to the chaos in spectroscopy in 1912 before the introduction of the Bohr hypothesis. Undoubtedly, the next two decades will witness just as rapid development in the extension or adaptation of these ideas to the solid state. With this development will come applications of practical value to the metallurgist.

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Hardness of Copper, and Meyer's Analysis

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THE hardness of annealed copper has been given in the literature and is easily obtained by any of the standard methods of hardness testing. It is not our intention to correct published values or to add to them, but to describe tests of two bars of annealed electrolytic copper in which the methods of Meyer's analysis were employed.

MEYER'S ANALYSIS OF BALL INDENTATION TEST

The ball indentation test is probably the most valuable hardness test we now have but, as it is carried out in the Brinell or Rockwell test, the result may be seriously in error without the operator suspecting such to be the case. This condition results from the isolated and uncontrolled nature of the measurement. The accuracy depends on the accuracy of the equipment and the care and skill used in the operations; there is nothing in the impression diameter, which is all that is measured, to indicate the presence of error. Meyer's analysis supplies a control of the measurements that goes far toward eliminating unsuspected errors.

The principles of this work may be obtained from elsewhere.¹ As this subject has not received the attention of this Institute, it may be well to summarize the more important points as follows.

The chief difference between the usual ball indentation hardness test and Meyer's test is the use of a number of loads, instead of one, covering the range from small to large loads. The reason for this may not be obvious; the resistance to penetration may, and generally does, vary with the penetration of the ball; consequently a single determination can give only the resistance at that particular load. At some other load, the resistance may be quite different. For example, a test on annealed copper at 250 kg. gave a resistance to penetration of 39.5 kg. per sq. mm., while a similar test at 3000 kg. gave a resistance of 56.8 kg. per sq. mm. For the purpose of finding some figure that might be used to represent the hardness of the sample of copper, there is no reason for selecting one of

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¹ Meyer: *Zeit. Ver. Deut. Ing.* (1908) **52**, 645.

Samuel L. Hoyt: *Trans. Amer. Soc. Steel Treat.* (1924) **6**, 396.

these figures in preference to the other. Both are correct, only one applies at low loads and the other at high loads.

How little one might know of the hardness of a metal from one observation is shown by the difference in these figures for annealed copper. The reason for this difference is to be found in the work hardening effect as the ball penetrates the sample. If all metals behaved alike in this respect, the problem of hardness testing would be much simplified, but, as Meyer has shown, the resistance of metals varies considerably with the load. The annealed metals of the ductile type show the greatest variation, while the plastic metals, and metals that have been considerably worked, show the least variation.

Meyer has also shown that the loads and the impression diameters bear a fixed relationship to each other. This is true irrespective of any variation in the resistance to penetration. This relationship will be discussed presently; it gives a control of the hardness determinations and supplies a means of checking their accuracy that cannot, from the nature of the situation, be secured with a single determination. Consequently, Meyer's analysis has the advantages of furnishing additional information and supplying an accurate control that do not come with the usual methods of carrying out the ball-hardness test.

The ball used in these tests is usually the standard Brinell ball, 10 mm. in diameter. If for some reason it is desired to use a larger or smaller ball, it is well to use one that, with the load in question, will have the same relationship between the load and the square of the ball diameter as is used with the 10 mm. ball. The loads range from 250, 500, to 3000 kg., and more. The number of loads selected for a given test would depend on the accuracy desired. Two determinations are sufficient theoretically but the accuracy will be increased by using four or even five loads.

The time of loading in the Brinell test is 30 sec. while no definite time is specified for the Rockwell test. Thirty seconds is not sufficient to allow the load to establish static equilibrium with the metal; in other words, the ball is usually still penetrating the sample at the end of the time interval. We have not found that any serious error (*i. e.* serious from the standpoint of the present state of the art of hardness testing) is introduced by neglecting the small change in the diameter of the impression that comes after the 30 sec. interval. The magnitude of this change for annealed copper at a load of 500 kg. is shown in Fig. 1. The data for this curve were obtained with a standard Brinell machine. The Brinell hardness number would drop 1.5 points by allowing the load to remain on for 1 hr. instead of 30 sec. Guillery has reported a variation in the hardness number of soft steel from 159 to 171 and of hard steel, from 212.5 to 227, because of neglect of the time factor.² It

² Guillery: *Compt. Rend.* (1917) **165**, 468.

may be permissible to neglect this factor, but by so doing we are bound to introduce an error. With annealed copper, 0.1 mm. at 500 kg. corresponds to about 35 kg.

The principal factors that influence the time of loading factor are the rate at which the load is applied, the character of the metal surface, and the condition of the surface. Thus Hankins has shown recently that the presence or absence of a lubricant on the ball and sample will lead to variable results.³ However, the necessity of eliminating the effect of the time factor depends on the requirements of the test; in the work described here, it has been eliminated and we believe that the results represent true equilibrium between the ball and the sample. The time required for this varies with the sample and the load, but for copper it is necessary to allow the load to act for at least 1 hr., while most of our determinations were made with a longer time of loading.

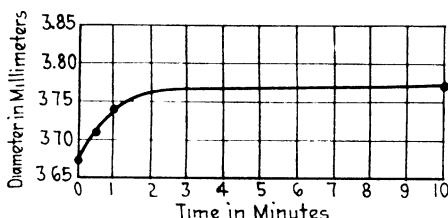


FIG. 1.—EFFECT OF TIME OF LOADING ON IMPRESSION DIAMETER FOR ANNEALED COPPER, USING A 500-KG. LOAD WITH A 10-MM. BALL.

The procedure thus far in Meyer's analysis has given a series of load-diameter determinations; in the present case, impression diameters at the loads 500, 1000, 2000, and 3000 kg. Meyer has shown that the relationship between the load and the diameter can be expressed by the equation

$$P = ad^n \quad (1)$$

where P is the load, d is the diameter, and a and n are constants. This relation is purely empirical, it having no known theoretical basis. It may be rewritten

$$\log P = \log a + n \times \log d \quad (2)$$

This being an exponential relationship, we should get a straight line by plotting the loads and diameters on log-log paper, and, in case the results are not in error, the points always fall on a straight line. It has been our practice to do this for all of our determinations; the reasons for doing so have been twofold.

First, an inspection of the formula will show that the constants may be obtained graphically, with great ease and accuracy, from the log-log plot. The constant a is the load corresponding to an impression diameter of 1 mm., while the constant n is the slope of the line. Such a plot is given

³ Hankins: *Proc. Inst. Mech. Engrs.* (1925) 1, 611.

in Fig. 4. Knowing the two constants is equivalent to knowing the whole course of the hardness curve, a curve from which the resistance to penetration at any load can be calculated. In this way, we can compare the hardness of two metals on a known and well-defined basis, or the hardness of a given metal in different conditions of heat or mechanical treatment. Such a comparison is not possible on the basis of any other ball indentation test that expresses the hardness as a single figure.

Second, it is only if the determinations are not in error that they will come on a straight line. If the time of loading has not been sufficiently long, for example, to eliminate the time factor, the impression diameter



FIG. 2.—MICROSTRUCTURE OF LOT 1. $\times 100$.

will be too small and, when plotted against the corresponding load, the point will be off. An error in loading will also give an incorrect diameter. Such errors may be readily detected and therefore eliminated by applying the methods of Meyer's analysis; and a check or control of hardness testing is obtained that is quite lacking with the ordinary methods.

We have referred to the variation in the resistance to penetration as the ball is forced into the sample. The initial resistance may be assumed to be given (perhaps arbitrarily) by the constant a as being the resistance at a load that produces very little deformation. The increase in this resistance as a result of the deformation during the test is evaluated by the constant n . Thus if n is equal to 2.0, the load varies as the square of the diameter; or, in other words, as the projected area of the impression.

The unit resistance to penetration does not vary in this case, no matter how deep the impression may be carried. If n is greater than 2.0, the load increases more rapidly than the projected area of the impression. This signifies that the resistance to penetration increases with the load. The constant n is, then, a numerical expression of the hardening effect that occurs, or which may occur, in the ball indentation test. These two factors a and n vary indiscriminately among the metals and must be known before the true hardness relationships of the metals will be understood. The lack of this knowledge has undoubtedly been responsible for much of the confusion and uncertainty that has always surrounded the ball test for hardness.

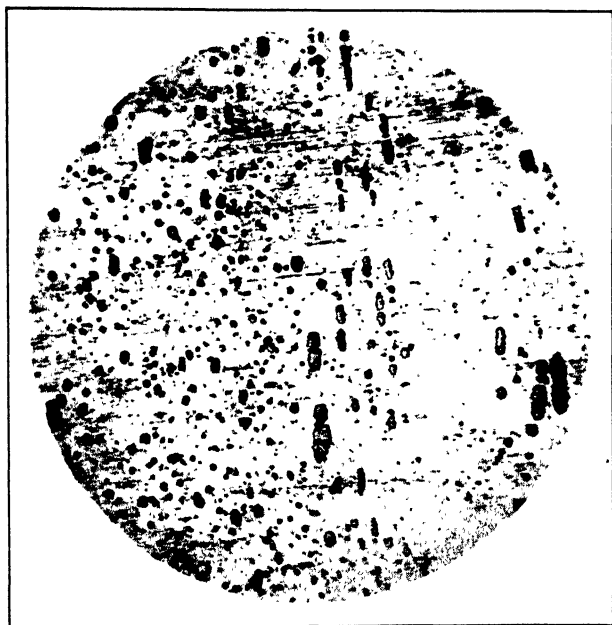


FIG. 3.—COPPER OXIDE IN LOT 2. $\times 600$.

Knowing the true manner in which the resistance to penetration varies in the ball test, it is natural to expect that the hardness number, selected to express the resistance, should vary accordingly. Meyer has shown that the Brinell number does not do so and that it is better to use the true mean pressure between the ball and sample. This is obtained by dividing the load by the projected area of the impression. This gives a number that remains constant when n is 2.0 and increases in accordance with the increased resistance to penetration when n is greater than 2.0. When we examine the Brinell number we find that even though the resistance to penetration remains constant for all loads, the Brinell number varies with the load. On the other hand, even though

the resistance increases considerably (as with copper) the Brinell number remains essentially constant over quite a range of loads. Obviously the true resistance to penetration, and hence the hardness, is not given by the Brinell number because the Brinell number depends partly on the geometry of spherical surfaces. This artificial character of the Brinell number introduces a variable error in hardness testing. For many purposes, considering the present state of the art, this error does no harm, but we feel it is desirable at least to appreciate the true character of the two tests (Brinell and Meyer) and be prepared to utilize the advantages of each.

Kürth followed the change in the constants a and n on a bar of annealed copper as it was stretched in tension up to the breaking point.⁴

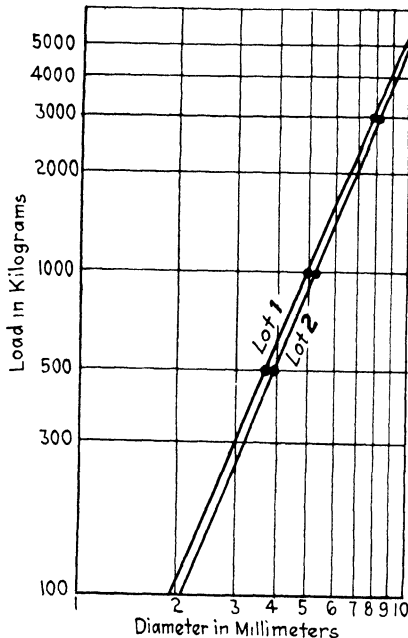


FIG. 4.—LOG-LOG PLOT OF MOST PROBABLE VALUES OF LOTS 1 AND 2 OF ANNEALED ELECTROLYTIC COPPER.

At various points, the bar was removed from the testing machine and a series of load-diameter relationships determined, from which the constants were obtained. In this way, he found that a increased somewhat as the hardness does in cold rolling and that n decreased from its high initial value to 2.0, at the breaking point, which corresponded to a 40 per cent. elongation. This is apparently the minimum value to which this constant can fall, at least with the common or ductile metals. The significance of this fact is, as we interpret it, somewhat as follows: At the outset,

⁴ Kürth, *Zeit. Ver. Deut. Ing.* (1908) **52**, 1560.

the annealed copper is potentially capable of being hardened, or strengthened, on being deformed. Consequently the first elongations harden the metal, which fact is reflected by the increase in a . Accompanying this change is a drop in the hardening ability of the metal, which is reflected in the decrease of n . This procedure continues up to the breaking point.

On analyzing this behavior in detail, we can imagine the elongation to be divided into unit steps, each step occurring over a small portion of the length of the bar. A small deformation of one of these units results in a decreased cross-section and consequent increase in unit stress. But such a deformation is accompanied by an increase in the resistance to deformation and, in spite of the increase in the unit stress, deformation is automatically transferred to neighboring portions of the bar. These, in turn, become deformed and strengthened and they pass the deformation on to other sections. Each deformation results in an increased a and decreased n until some section of the bar loses its ability to become further strengthened by deformation ($n = 2$). Then the increase in unit stress is no longer accompanied by an increase in resistance; necking starts and fracture occurs at that point.

Metals with this characteristic are able to deform considerably before rupture occurs and they are classified as ductile, and the constant n becomes the numerical expression of the ductility. The deformation is general in that it extends over the entire length of the bar. From the work of Kürth, we know that fracture occurs as soon as n drops to 2.0, which is in good agreement with the loss in hardening power at this point.

After having set up this picture of the elongation of the ductile metal, we decided to test it out as follows. If a metal with a high initial n value deforms generally, *i. e.*, with a considerable decrease in the average or general diameter, then a metal that has been cold worked and had its n value reduced to about 2.0 should break with correspondingly less general deformation. Our test of the point was to be the general reduction in diameter; this was chosen in preference to the elongation to avoid the error due to the deformation at the necked portion. For the test we selected two samples of copper wire, one in the annealed condition and one after cold drawing to give a 19 per cent. reduction. The former was 0.030 in. in diameter and the latter (a section of the former wire that had been drawn) was 0.027 in. in diameter. Both wires were broken in tension and their average, or general, diameters again measured. The annealed wire was found to be 0.0264 in. and the cold-drawn wire 0.0267 in. in diameter. The latter wire had almost lost its ability to elongate and its ductility would be said to be low. It is interesting to note that wire drawing should have little effect on the reduction in area in the tensile test for the metal is always in the same condition at the point of fracture ($n = 2.0$) whether the wire initially were annealed or cold drawn,

A verification of our own work is given by the published data covering the variation of the per cent. elongation in the tensile test during wire drawing. The fall is very rapid with the first reductions and agrees well with the change in n over this range. This is one of the most striking changes produced by wire drawing but is readily to be accounted for by the reasoning suggested by a study of Meyer's constants. On the other hand, this drop in ductility has no effect on the plasticity or its ability to flow under pressure. The metal simply is not hardened materially by such deformation.

After considering the results of the investigation reported we shall give another application of Meyer's analysis, by which results on the effect of cold rolling on the hardness of a metal, such as those of Rawdon and Mutchler, can be verified and be placed on a sound basis.

HARDNESS OF ANNEALED COPPER

Having indicated the line of attack employed in this study, we may turn to the data obtained. Our results agree well with Norbury's⁵ and the results of both series agree well with the early work of Meyer and Kürth. That is, while copper is a soft metal with an a value of between 15 and 22, it hardens considerably on being deformed, with an n value of around 2.4. Our work differs from that of Norbury in that he used a 30 sec. loading, while we used not less than 1 hr., or sufficient time to give static equilibrium. Norbury has shown that the time of loading may have a marked effect on the constant n^6 and we wished to eliminate this effect entirely.

Norbury paid particular attention to the effect of annealing on the constants a and n and found that a certain hardness figure— $\log a + n$ —remained constant for the different annealing treatments. If this figure is examined, it will be seen that it is equal to $\log P$ when $\log d$ is unity. In other words, his figure remains constant for all annealing treatments when the determination is made at an impression diameter of 10 mm., or the load required to produce an impression of 10 mm. remains constant.

While the figure mentioned remains constant in Norbury's investigation, such a figure does not remain constant in the early work of Meyer and Kürth nor in our own work. This shows that it does not remain constant under all conditions. On the other hand there seems to be good reason for believing that there is some impression diameter, real or fictitious, at which the hardness remains constant, or nearly so, for different conditions of heat and mechanical treatment. This hardness would be the hardness that a metal approaches as a limit when work hardened, or its ultimate hardness. It is the hardness at the opposite

⁵ Norbury: *Jnl. Inst. Met.* (1923) No. 1, 407.

⁶ Norbury: *Trans. Faraday Soc.* (1923) **19**, Pt. 1.

end of the hardness curve from the hardness at a , when the constant a is determined for the dead soft annealed metal. This is but another reflection of the variability of the hardness of metals and indicates the necessity of measuring the property under known and well defined conditions.

COPPER USED

As material for this study, we selected two bars of hot-rolled electrolytic copper, one from each of two sources. Supposedly, these represented the standard electrolytic copper on the market in this country of the grade used in the electrical industry. They are designated here as 1 and 2. The results of the spectrographic analysis are given in Table 1.

TABLE 1.—*Spectrographic Analysis of Lots 1 and 2*

Element	Lot 1	Lot 2
Nickel.	Nil	Nil
Aluminum.	Trace	Trace
Manganese	Nil	Nil
Silicon	Faint trace	Faint trace
Iron..	Present	Present
Tin	Trace	Nil
Calcium	Trace	Trace
Leads	Nil	Nil
Silver	Nil	Nil

The results of the ordinary chemical analysis are given in Table 2.

TABLE 2.—*Chemical Analysis of Lots 1 and 2*

Element	Lot 1	Lot 2
Fe	0 0018 %	0 0025 %
Ag	Nil	Nil
Pb	Nil	Nil
As.	Traces	Traces
P.	Traces	Traces
Cu ₂ O	0.138 %	0.216 %
CuS..	0 007 %	0.01 %

One-half of each bar was annealed at the metallurgical laboratory of the Testing Laboratory and the other half at the wire plant, along with other commercial work. The annealing temperature was 600°C., while the bars required $\frac{1}{2}$ hr. to come up to temperature and were held at temperature for $1\frac{1}{4}$ hr. After this, the bars were quenched in water. A water-sealed and electrically heated Kenworthy furnace was used in this work. The two lots were examined under the microscope, as a matter of routine. They were found to be normal, except that Lot 2

seemed to have considerable copper oxide. The chemical analysis shows that there is not enough present to hurt the copper. Fig. 2 shows the structure of Lot 1, and may be taken as representative of Lot 2 as well, which is not reproduced here, as the grain size was about the same as shown. Fig. 3 represents the unetched micro-section of Lot 2, polished to bring out the oxide. Lot 1 showed less oxide than is represented in Fig. 3.

HARDNESS MEASUREMENTS

Instead of the usual Brinell machine, we used a 10-ton Olsen testing machine for applying the loads; with this it is a simple matter to apply and maintain constant for any length of time any load up to 9000 kg. A special holder, designed by T. S. Fuller of this laboratory, was used to hold the ball and sample. The balls were of the kind generally used in ball testing, of 10 mm. diameter. The impression diameters were measured with a comparator and are believed to be accurate to 0.01 mm. Impressions were made at four places, about $1\frac{1}{2}$ in. apart, and at the loads 500, 1000, 2000, and 3000 kg. The data obtained are given in Table 3.

In each case the load-diameter values were plotted on log-log paper and found to satisfy the straight-line requirement with reasonable accuracy. From these lines, the constants a and n were determined graphically. In all respects, the two lots of copper differed in hardness values and, as will be shown later, these differences were not due to variations in the experimental procedure. No consistent differences were found that could be ascribed to a difference in the annealing treatment used. The variations shown in Table 3 must, then, be due to variations in the resistance to penetration at the various points selected for the impressions and to the experimental error of the observations. In this state, the data do not give a precise evaluation of the difference in hardness between the two lots.

MOST PROBABLE VALUES

The impression diameters agree among themselves fairly well, so that an average diameter should be very close to the true diameter in any case. Even so, there are a few exceptional values that seem to fall outside of the experimental error and, even though they are not in themselves in error, they should be eliminated from a figure that is to represent the particular lot of copper. Consequently we have plotted the values on probability paper; because of the general consistency of the data, the points fell on a straight line with a small slope.

On first plotting the impression diameters on the probability paper, both lots of copper were combined. These points gave two lines, instead of one, with a vertical break at the 50 per cent. point. All the measure-

TABLE 3.—*Impression Diameters of Annealed Copper*

Impression	*500 Kg.	*1000 Kg.	1500 Kg.	2000 Kg.	3000 Kg.	a	n
Lot 1, Annealed by Factory							
A	3.73	4.95	5.91	6.65	7.84	21.0	2.39
B	3.74	4.99		6.60	7.93	20.7	2.37
C	(3.70)	5.00		6.62	7.95	21.8	2.39
D	3.76	(5.01)		6.66	7.91	21.0	2.40
Av.	3.74	4.99		6.63	7.91	21.1	2.39
Lot 1, Annealed at Testing Laboratory							
A	3.83	4.98	5.92	6.59	7.96	20.5	2.41
B	(3.70)	4.95		6.67	7.94	22.0	2.36
C	3.71	4.97		6.65	7.81	21.8	2.37
D	3.65	4.96		6.62	7.93	21.4	2.38
Av.	3.72	4.96		6.64	7.91	21.4	2.38
M. P.	3.72	4.975	6.63	7.93	21.2	2.38	
Lot 2, Annealed by Factory							
A	3.95	5.24	6.19	7.02	8.22	17.5	2.45
B	3.95	5.25		6.95	8.18	16.5	2.47
C	(3.95)	†(5.24)		6.96	8.20	16.5	2.46
D	3.98	5.20		6.92	8.05	15.9	2.48
Av.	3.96	5.23		6.96	8.16	16.6	2.46
Lot 2, Annealed at Testing Laboratory							
A	3.92	5.21	6.18	6.97	8.23	17.3	2.44
B	3.93	5.16		6.93	8.20	17.5	2.43
C	(3.96)	5.27		6.95	8.22	16.5	2.45
D	3.97	5.18		6.93	8.13	15.0	2.52
Av.	3.94	5.20		6.94	8.19	16.6	2.46
M. P.	3.95	5.21	6.95	8.20	16.7	2.46	

* The numbers in parentheses were obtained from the log-log plot. The impression diameters are all in millimeters. Av., these are average values for each bar. M. P., these are the most probable values for each lot.

† The load was 1090 kg., impression was 5.45 mm.

ments from one lot were below 50 per cent. and the others above 50 per cent. This showed that the two lots would have to be considered separately. It seems probable, however, that the use of a large number of lots would give values around some most probable value and that by following up this line of attack, one would be able to arrive at the true effects of the

common constituents of copper and the annealing treatments to which they are subjected. This should give better values than those obtained from a comparatively few observations on graded series in which the constituent in question is allowed to vary over the range being studied. In the present case, there is no necessity of separating the two bars of one lot and the values given may be taken as closely representative of these two materials.

The most probable values of the impression diameters for the loads used are plotted on log-log paper in Fig. 4. These two curves may be taken as typical of such plots and they show that Meyer's relationship between the load and the impression diameter holds over this range. We have carried the loads much higher, even up to 9000 kg., and found the relationship to hold up to approximately the load required to impress the ball up to its full diameter. The lower limit to which this relationship holds is not known with precision.

SUMMARY OF HARDNESS DATA

The hardness of these two lots has also been determined by the Brinell hardness testing machine (using one of the hydraulic type) the Rockwell hardness tester, and the scleroscope. These results are given in Table 4. The Brinell hardness number, as usually determined, represents one isolated determination. If a number of checks are made, an error is introduced as the result of variations in the hardness from place to place on the bar. In the work described here, we are able to arrive at a better figure for the Brinell hardness by using the impression diameter at 500 kg. on the log-log lot. This value depends not alone on the single determination at 500 kg. but on the other determinations with which it must be consistent. The Brinell numbers obtained by using the impression diameters from the plots in Fig. 4 are included in the table. These figures indicate that the copper of Lot 1 is harder than the copper of Lot 2. An inspection of the log-log plots shows that at some higher load, the impression diameters of the two lots will be equal, *i. e.*, at the point of intersection. In this case, the intersection comes at a purely fictitious load for the load would lie above that required to cause the ball to penetrate to its full diameter. However, we are inclined to believe that even such a fictitious intersection has a certain significance for it shows that one metal hardens at a more rapid rate than the other. In the Brinell test, the deformations may not be severe enough to cause the initially softer metal to overtake the harder metal, but as long as that is its tendency, some other mode of deformation may indicate that the supposedly softer metal is actually harder, or else that the two metals are equally hard. These points may well be borne in mind when considering the results of the common hardness tests.

TABLE 4.—*Hardness of Annealed Copper*

Lot	<i>a</i>	<i>n</i>	Brinell Hardness Number		Scleroscope Number	Rockwell Hardness Number
			1	2		
1	21	2 39	44 4	43 6-44 9	8	27
2	18	2 42	39 1	40.2-42.4	7	25

NOTE.—The Brinell hardness number was determined with a 500-kg. load and a 10-mm. ball. The figures in 1 correspond to the most probable values for an indefinite time of loading, and those in 2 were obtained with a Brinell machine with a 30 sec. loading. The scleroscope number was obtained with the universal hammer. The Rockwell numbers were obtained with the $\frac{1}{8}$ -in. ball and 100-kg. load, on the B scale. The pointer was allowed to come to apparent rest before the load was released.

The *a* and *n* values of this table give the same information as has just been considered. The hardness curve of Lot 1 starts off at a higher point than that of Lot 2, as is shown by the greater *a* value. However, its slope is less, so that the two curves will intersect. A comparison of these two metals as to hardness will depend on the load used to measure the property. If the *n* values were the same, the comparison would be independent of the load and the readings at 500 kg. would be strictly accurate.

MEYER'S ANALYSIS AND COLD-ROLLED COPPER

Rawdon and Mutchler recently reported on the variation in hardness due to cold rolling.⁷ They stated that the hardness was shown to decrease as soon as the reduction was carried above about 50 per cent. The methods of Meyer's analysis offer a control of determinations of this kind that seem to be capable of differentiating between true and false conclusions regarding the hardness of the samples drawn from the data obtained from the tests.

Kürth has shown⁸ that the constant drops from above 2.4 to 2.0 in the tensile test. We have shown that *n* remains constant at 2.0 if the deformations are carried above that reported by Kürth, of 40 per cent. elongation. There is no evidence of which we are aware to indicate that *n* does not remain constant over the higher reductions. In other words, we are dealing with a constant *n* over those reductions that are supposed to produce softening. Such being the case, a softening would have to be caused by a decrease in *a*. This suggests the desirability of determining this constant, for it is the only known factor that could be responsible for such a softening, as long as *n* remains constant. From the theoretical mathematical point of view, a decrease in *n* below 2.0 would lead to the same results when the hardness determinations are made at impression diameters greater than that which corresponds to *a*.

⁷ Rawdon and Mutchler: *Trans.* (1924) **70**, 342.

⁸ Kürth: *Zeit. Ver. Deut. Ing.* (1908) **52**, 1560.

But we have no evidence that such occurs and an assumption that it does would be extremely improbable.

A typical example of a treatment that lowers the a of cold-worked metals is the annealing used to soften the metal. The constant a falls from around 80 to around 20. The n value rises from 2.0 to that of annealed copper, so that the softening is due to the decrease of a . Had Rawdon and Mutchler determined these constants and found them to vary as just suggested, the effect would be at once accounted for as the result of an annealing effect that had unknowingly occurred during the operations.

Another check that could be used would come from plotting a series of load-diameter determinations on log-log paper. If the conditions of the test were such that accurate and reliable readings could not be obtained, an indication of such a condition would probably appear. We are referring particularly to the circumstance that the sample being tested may be too thin. While we have not thoroughly tested the point, for it has not arisen seriously in our own work, the following may throw some light on to the question.

In one test we used a strip of cold-rolled copper 0.099 in. thick. This was selected because previous tests had indicated that a sample of this thickness would be too thin for reliable readings, and we wished to bring out the effect of the thickness of the sample clearly. As usual, a series of impression diameters with a 10-mm. ball was determined for a number of loads and the results plotted on log-log paper. The points held fairly well to a straight line up to 3000 kg. although the impressions came through to the underside. Higher loads came off the line and the test was palpably improper. The a value was slightly low at 75, but gave no strong indication that the readings were in error. The n value was 1.935, or well below the constant value of 2.0 which had been obtained for cold-rolled copper. This could be due only to excessively large diameters at the higher loads, for the line started at the proper point. The diameters being too large, the hardness numbers determined from them must be too small. We assume this to be the so-called "anvil effect."

The same point was also tested with the Rockwell tester with thin strips, when the same behavior was observed. The ball, on being loaded, forces the metal to flow up around itself and the strip actually comes up off the support. The impression diameter is too large and, as a basis of a hardness test, has a purely illusory value. The beginning of this anvil effect is evidenced by a small drop in the hardness number and, on samples that are only slightly too thin for reliable tests, may be difficult to detect. One determination seems to be quite unreliable for use in discriminating between a true and a false hardness number, in fact the hardness at real low loads may not be in error. It was only by determining the whole course of the hardness curve that a positive clue was found and that came

from an n value known to be in error. From our own work we believe that the anvil effect is responsible for an apparent softening of cold-rolled strips and that the point at which it makes its appearance will depend on the thickness of the strip, the ball diameter, and the load used in the hardness test.

The conclusion to be drawn so far is that such a softening as was reported by Rawdon and Mutchler has been neither proved nor disproved. The evidence they present fails to show that such an effect is probable but, by the same token, the evidence of other workers (including our own) also fails to prove that such an effect is impossible. We believe, however, that the preponderance of the evidence points to some condition during rolling or in the procedure used to test the hardness of the strips, as being responsible for the abnormal values. The manner in which the methods of Meyer's analysis may be utilized to indicate the source of the trouble or else to place the results on an uncontrovertible basis have been given.

DISCUSSION

C. S. WITHERELL, New York, N. Y. (written discussion).—Referring to the equation $P = ad^n$ that the authors quote from Meyer's work: While it is true, as the authors state, that this relationship is purely empirical nevertheless even an empirical equation should be rational in certain respects. Many engineers who have developed empirical equations for approximately showing physical relationships have failed to investigate the applicability of their equations over extended ranges.

Let us call p the bearing strength of the metal expressed in kg. per circular mm. of horizontal area of dent; then can be derived from Meyer's equation $p = \frac{P}{d^2} = ad^{n-2}$. It can be seen that this latter equation would give the initial bearing strength (*i. e.*, when P is infinitesimal) a value of zero, and in the other direction an ultimate value of infinity, when n is greater than 2.

It is quite obvious that whatever the load may be there must be a surface to support it and also the ratio of the area of the supporting surface to the load must be a definite value.

Imagine the load to be gradually applied, the authors have already pointed out that the bearing strength increases due to the hardening effect of the penetrating ball, hence the initial bearing strength must be that of the metal before such hardening took place. Irrespective of the shape and size of the loading surface the bearing strength can not exceed that of fully hardened metal. It is therefore evident that the graph showing the true relationship between applied load (abscissas) and bearing

strength (ordinates) is a curve that approaches a horizontal asymptote whose ordinate is the bearing strength of the fully hardened metal.

Of several plausible asymptotic curves the hyperbola is the simplest and lends itself to easy computation. The hyperbolic equation fitting our case may be written $p = M - \frac{C}{P + A}$ wherein M = the ordinate of the asymptote (which is horizontal), C and A are equational constants. This equation is also purely empirical and its acceptance would naturally depend upon how closely it gives values approximating the truth over an extended range. It is to be noted that the hyperbola expressed by the equation can be passed through three given points.

It can be derived from the before-mentioned hyperbolic equation that the initial bearing strength $p_0 = M - \frac{C}{A}$.

Referring to the accompanying graph (Fig. 5) the solid-line curve is that of equation $p = M - \frac{C}{P + A}$ passed through the three given points

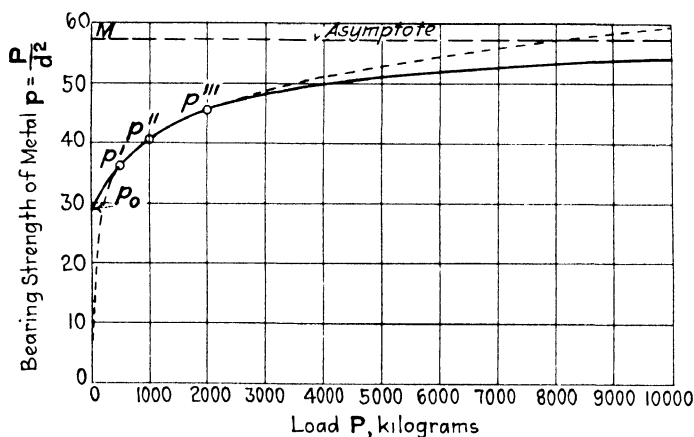


FIG. 5.—GRAPH SHOWING RELATION BETWEEN APPLIED LOAD AND BEARING STRENGTH OF METAL (EXPRESSED IN KG. PER CIRCULAR MM. OF HORIZONTAL AREA OF DENT).

p' , p'' , p''' . The dotted branches are of the curve $p = ad^{n-2}$ passed through any two of the given points and assuming that the third point fits, p_0 is the initial value of p . The horizontal broken line is the asymptote.

The slope of the tangent at p_0 is a measure of the initial rate of hardening. It can be determined by the equation $H_0 = \frac{\delta p}{\delta P} = \frac{C}{A^2}$ (at $P = 0$).

By using the "M. P." values given by the authors in their Table 3 the values given in the following table were computed:

	Lot 1	Lot 2
$p = \frac{P}{d^2}$ for $P = 500$	36 131	32 046
$p = \frac{P}{d^2}$ for $P = 1000$	40 403	36 840
$p = \frac{P}{d^2}$ for $P = 2000$	45 499	41 406
Asymptotic ordinate M	59 345	49 916
Equational constant C	51463	24371
Equational constant A	1716 9	863 8
Initial bearing strength p_0	29 371	21 702
Initial rate of hardening H_0	0 0175	0 0327

It is assumed that the information desired is the hardness of the metal before additional deformation takes place and apparently the p_0 value given by the hyperbolic equation is a fairly close approximation thereto. I tried other plausible asymptotic equations and found the p_0 value to seldom vary more than 1.5. The M value is not so dependable as a measure of the ultimate hardness although it may be of relative significance in comparing similarly prepared specimens. Naturally the way to determine the ultimate hardness is to specially harden a specimen for that purpose. Of greater significance is the value H_0 .

Referring to the authors' Fig. 3, microphotograph showing the copper oxide in Lot 2, on account of the excessive amount of oxide shown I would prophesy that Lot 2 would need more frequent annealing than Lot 1 for its proper working. The calculated initial rate of hardening H_0 is nearly twice as much for Lot 2 as for Lot 1 which I interpret indicates the same thing.

If an asymptotic assumption be used for calculation the initial hardness and the initial rate of hardening then the three loads P' , P'' , P''' , should be chosen so as to give minimum errors as follows: P' should be as low as possible consistent with producing a dent that can be accurately measured (say 1 to 2 mm. diameter). P''' should be as large as possible without giving a dent whose diameter is more than $0.7 \times$ diameter of ball; a greater dent-diameter would introduce excessive wedging effect on the steep surface of the ball. P'' should be chosen say $\frac{1}{3}$ or $\frac{1}{2}$ way from P' to P''' .

By choosing three points on the authors' log-log plot of $P = ad^N$, *e. g.* $P = 500$, 1000 and 2000, and determining the corresponding M , C and A values, then superimposing a log-log plot of $d =$

rived from $\frac{P}{d^2} = M - \frac{C}{P} + A$ upon the authors' plot there will be found a very close match of the curves between the points $P = 200$ and $P = 3000$; outside of those points the two curves perceptibly diverge, the lower branch of the new curve bends to the left and the upper to the right, the slope of both branches gradually approach 2.

The authors have shown that the log-log plot is an excellent means of determining the dependability of the results obtained with the commonly used loads, but their equation fails to give the hardness of the unaltered metal.

I would like to ask the authors why the ball is generally used in preference to the conical point. I can understand why the 90° point recommended by Ludwik is not satisfactory due to the point being easily upset or shattered and also due to the excessive lateral flow of the metal under test produced by the wedge-effect of the entering point. What I have in mind is a very obtuse point, say 150° , which would obviate these difficulties and even permit making the loading-point of some extremely hard material such as fused corundum (synthetic ruby or sapphire). The fact that the dent produced by a conical point remains constantly of the same geometric shape and that the ratio between the average-depth of indentation and dent-diameter remains constant commends it over the spherical surface.

S. L. HOYT AND T. R. SCHERMERHORN (written reply to discussion).—The main part of Mr. Witherell's discussion relates to the utilization of mathematical analysis to secure information from experimental data. At the outset, it is suggested that we have failed to extend our own analytical work over sufficiently extended ranges and that we have therefore failed to secure all of the information which is contained in our data. While we agree most heartily with the general position of Mr. Witherell as to the use of mathematics for these purposes, we can not concur in his treatment of the data submitted in the paper.

First of all, the exponential relation of Meyer has been found to fit the experimental data with great-exactness over the range of loads corresponding to impression diameters of 1 mm. and 10 mm. for a 10-mm. ball. If any other relation or equation is proposed for use, the first requirement which it must meet is that it fit the data with equal accuracy. This point seems to be quite completely neglected in Mr. Witherell's treatment.

To treat this in more detail, let us first take the lower portion of his plot in which the exponential and hyperbolic relationships are both plotted. The former is known to hold down to a load of about 20 kg. or an impression of 1 mm. This would be to the load of 20 kg. per circular mm. on the plot. From this it is at once obvious that the hyperbolic relation does not hold here and therefore that the initial bearing strength p_0 of Mr. Witherell is seriously in error. For example, from the hyperbolic plot the impression at a load of 20 kg. per circular mm. would be vanishingly small, but it is actually about 1 mm.

To turn now to the course of the relation at higher loads, we would point out that the relation $P = ad^n$ holds up to an impression diameter of 10 mm. which comes at a load of about 5000 kg. The divergence of the hyperbola from the exponential curve shows that Mr. Witherell's rela-

tion does not hold at these high loads. The extension of any relationship above the point at which the ball sinks to its full diameter, gives purely fictitious values. A discussion of this point, as well as the bearing strength of cold rolled copper, is given in our current Institute of Metals paper and we would refer those interested to that place to avoid repetition.

Mr. Witherell and others have raised the point of measuring the hardness of the unaltered metal. We feel that that is a rather paradoxical question, or that the use of the test for such a purpose violates the fundamental principle of the ball hardness indentation test which is designed to measure what may be termed the "plastic" hardness of metals. If one wishes to measure the "elastic" hardness, the logical method is the classical test of Auerbach. This would avoid the questionable procedure of extrapolating beyond the limits of the experimental data.

A reply to the suggestion of using a cone instead of a ball for an indenter has been given in the oral reply. As to the wedging effect in impressions above 0.7 of the ball diameter, we would point out that our procedure of allowing the load to remain on until static equilibrium is reached eliminates it and that we get correct impression diameters up to about 10 mm. with a 10-mm. ball.

While we are unable to concur in Mr. Witherell's proposed treatment of our data, and for the reasons stated above, we feel that the effort to extract full information from experimental data by the methods of mathematical analysis is always to be attempted.

S. L. HOYT (in reply to C. S. Witherell's question re conical point).—The main consideration here is that the ball is actually used in hardness testing. Consequently, it is very interesting to investigate the conditions during ball hardness testing. If the cone test were as universally employed as the ball test, undoubtedly more attention would be paid to it. But there is another consideration, which is that the resistance to penetration in the case of the cone remains constant for different loads; it does not depend upon the depth of penetration.

It is well known that annealed copper hardens on being deformed; in other words, a test should be so devised as to bring out this work hardening, and if the cone test fails to reveal it, that simply indicates that the cone test automatically eliminates one of the constants or one of the variables from the test. On that account the ball test is capable of bringing out more information regarding the resistance to penetration of annealed copper than the cone test. Therefore, for both practical and theoretical reasons, it is well to investigate the ball test in preference to the cone test.

C. S. WITHERELL.—Do you think that would be true if the cone were blunt, say, 150° angle?

S. L. HOYT.—Meyer tested that point out very carefully, as you will see in his original paper in 1908. In that work, as I remember it, he used

cones of different angles, and the striking feature of that particular part of his investigation was that the resistance remains constant in spite of the increased deformation produced.

C. R. HAYWARD, Cambridge, Mass.—It is well known that one of the criticisms of the Brinell hardness test is that the material gradually grows harder as the ball penetrates the specimen, and there has been considerable interest in developing a method which would overcome that objection. There are many who believe that the Rockwell machine is greatly superior to the Brinell machine on that account.

It seems to me that Mr. Witherell's point anent the authors' formula is very well taken, that the assumption of no resistance at the start is purely an assumption, and that if we are developing a mathematical formula we certainly should take cognizance of the extreme ends of the curve. For practical work, no doubt the method proposed by the authors is wholly satisfactory for anything within the accuracy of ordinary testing.

W. H. BASSETT, Waterbury, Conn.—The Brinell method of hardness testing is very important, and this method of checking up the accuracy of the hardness tests is undoubtedly of value.

C. H. DAVIS, Waterbury, Conn.—Probably all who have made tests with the Rockwell and Brinell machines have noted that an error, due to the length of time in testing, is liable to creep in because of the fact that in most laboratories there is considerable vibration. That is particularly noticeable with the Rockwell machine, where the load is applied and remains suspended on the lever after the approximate hardness is reached. If the sample has a hardness of approximately 90, the dial pointer comes to rest very quickly and thereafter moves slightly. With soft metal like copper, the dial makes perhaps $1\frac{1}{2}$ revolutions, and comes to rest slowly, and the longer the load is left on, the farther the pointer goes on the dial, indicating continued depression. If you tap the bench with the finger, the dial continues to move, showing increased loading, not in actual weights, but due to vibration either of the building or of working parts in the building. In laboratory practice it is well to mount the machine upon a rubber cushion. It would seem inadvisable to stop the test at an early point; that is, within a few seconds after the load has been applied.

An A. S. T. M. paper published in 1917⁹ showed that there was no increase in the Brinell hardness of soft brass after even 5 min. loading.

S. L. HOYT.—Our work was done on an Olson testing machine, using a special holder for the specimen and ball. As far as we were able to detect, this vibration effect, which is so pronounced with the Rockwell machine, was quite absent. The load was allowed to remain on for more than 1 hr.; as a matter of fact, we frequently left the load on for 6 to 8 hr., or even more, sometimes overnight, with the idea of getting true static equilibrium between the load on the ball and on the sample. We feel that there is

⁹ Testing of Sheet Brass (1917) XVII, Part II.

no error due to vibration or other sources there, such as the condition of the surface, and so on.

We also found, with the Rockwell machine, that vibrations do play an appreciable role. If you tap your finger on it, the pointer moves around, and the checks which we were able to get with the Rockwell machine were very, very poor, as compared with the checks that we were able to get with the Olson machine, using the 10-mm. ball on the larger-size samples. So that for a method of testing or investigating the property of hardness, it is our opinion that a machine of the Olson type should be used, and that the Rockwell machine or the ordinary Brinell machine would be quite incapable of giving you the results which you want.

C. H. DAVIS.—Does not the part that the specimen rests upon have a great deal to do with it?

S. L. HOYT.—Yes, I think so. In our work, the sample rested on steel.

C. S. WITHERELL.—In the Olson testing machine you have a very heavy base which probably absorbs the vibration before it can be transmitted to the surface of the ball, a thing which you do not have in the Rockwell machine.

S. L. HOYT.—We are also presenting a paper before the British Institute of Metals on "The Hardness of Cold Rolled Copper," which carries this idea over into that field. In that paper we report on the variation in the hardness over the cross-section of a rolled bar of copper, using the Rockwell machine. The Rockwell hardness number, we will say, averaged about 38, for the conditions used, and if we were able to get checks within plus or minus 5 points with the Rockwell, we considered we were pretty well off. In other words, there was considerable variation in the results.

Speaking now of the impression diameter, we would not be satisfied with results that vary more than 0.02 or 0.03 mm. That is, the accuracy which you are able to obtain with the methods discussed here is of a different order of magnitude as compared with the accuracy obtained with the Brinell or Rockwell.

I believe that Meyer's method of analysis is not applicable to ordinary hardness testing and we do not use it. But in the case of the work which Rawdon and Mutchler reported here 2 years ago, in which the effect of rolling upon the hardness was discussed, I believe the methods of Meyer's analysis are indispensable. The ordinary hardness test seems to be quite incapable of giving a satisfactory answer to the question involved, and the use of the Meyer's analysis in that case would either place the results of Rawdon and Mutchler on an uncontrovertible basis or else would indicate the source of the error which may be involved in their work. The method of Meyer's analysis I think gives us a tool which is far superior to

the ordinary methods of hardness testing in case the property itself is under investigation.

Meyer's relation is a purely empirical relation; it has no theoretical basis. It is stated in our paper as an exponential relation. It could be stated as any other mathematical relation which would fit the experimental data. The application of this equation does not go much below 1 mm. in diameter (it was carried down to some 0.9 mm.). What may happen below 1 mm., I do not believe has ever been brought out.

As for the upper portion of the curve, we can say, on the basis of our own work, that it holds for annealed copper up to practically 10 mm. in diameter, also on annealed steel, and we presume on other material. It holds up a load which is sufficient to impress the ball up to its full diameter. Any loads above that have a purely fictitious meaning. I am not clear in my own mind how much value a mathematical analysis would have in case the loads are carried above that point.

The Effect of Lead and Tin with Oxygen on the Conductivity and Ductility of Copper

BY NORMAN B. PILLING,* BAYONNE, N. J., AND GEORGE P. HALLIWELL,† EAST PITTSBURGH, PA.

(New York Meeting, February, 1926)

The effects of lead and tin up to maximum contents of about 0.1 per cent. each, in the presence of oxygen between 0.04 and 0.30 per cent., have been studied. Tin is retained efficiently in the oxidized condition, whereas lead is not. An approximate relation between the lead-oxygen and tin-oxygen contents is deduced which, if observed, permits the presence of these elements without detrimental effect. Excess of lead beyond this limit affects ductility and rolling properties adversely and an excess of tin correspondingly diminishes the conductivity. It is shown that copper carrying a combined lead and tin content of several hundredths per cent., yet fully equal in quality to electrolytic wirebar, may be produced under commercial conditions.

TIN is not normally found in more than bare traces in current grades of American electrolytic copper, and lead is rarely found to more than a few thousandths per cent. In the electrolytic refining of copper these metals do not present great difficulty in separation and their presence in any considerable amount in copper that has been refined by this method need not be tolerated. On the other hand, the effect of these elements is not entirely academic, as a considerable tonnage of scrap copper liberally contaminated with them has been reclaimed by the fire-refining process into metal with a residual lead and tin content of several hundredths per cent., yet having excellent working properties and fully equal in quality to current grades of electrolytic wirebar. Such copper has been found entirely suitable for use in the manufacture of electrical apparatus.

In the absence of oxygen, tin is known to depress the conductivity rapidly, and lead to impair ductility and the rolling properties, yet the effects of these metals on commercial grades of copper—*i. e.*, copper containing from 0.03 to 0.10 per cent. of oxygen—apparently has not received systematic attention. Occasional reference is made to the fact that in the presence of oxygen lead may be tolerated, yet Addicks says,¹ in regard to overpoling: "The unstable condition can be controlled by adding certain substances, notably lead, in small quantities, but as mere

* The International Nickel Co.

† Research Dept., Westinghouse Elec. & Mfg. Co.

¹ L. Addicks: "Copper Refining," 132. McGraw-Hill Book Co., Inc., New York. 1921.

traces of lead make copper brittle the cure is worse than the disease." An adequate guide to the scattered and fragmentary literature of the subject is given in *Circular 73* (p. 53) of the Bureau of Standards (1922).

It is the purpose of this paper to present some experimental results obtained at the Westinghouse Elec. & Mfg. Co., showing the effects following the introduction of these elements into copper at several different levels of oxygen content. Although realizing fully the value of a closely controlled and rigorous experimental technique, such as is being followed at the present time in England at the National Physical Laboratory on a fundamental study of the effects of various elements on copper, it has been felt that perhaps a more direct approach approximating commercial conditions would have results of some value. It was found convenient to approach the problem in two steps:

1. A scrutiny of the effects of comparatively large (0.1 per cent.) additions of lead and tin to a base melt of fire-refined copper carrying a small initial content of these metals.

2. A comparison of properties between copper free from lead and tin, and copper containing relatively small amounts of lead and tin, in wire-bars containing about 0.07 per cent. of oxygen.

ADDITIONS OF LEAD AND TIN

In carrying out the first phase of this program a 50,000-lb. heat of copper in process of refining was used. During the poling period the bath constituted a source of copper of which the oxygen content gradually diminished, lead and tin remaining at a minimum. After $1\frac{1}{2}$ hr. of poling, the process was interrupted for about 10 min., eight 15-lb. ladles were withdrawn in succession and to them certain additions of lead and tin were made. These additions had previously been prepared as single pieces of the metals; they were lashed with copper wire to an iron rod, plunged to the bottom of the ladle and stirred briskly for a moment. The ladle was then poured into a copper mold giving an ingot 2 by 2 by 8 in., weighing 10 lb. The series was composed thus:

- 1 ingot, no additions
- 3 ingots, 3 different lead additions
- 3 ingots, 3 different tin additions
- 1 ingot, lead and tin addition

Some variation in the weight of metal scooped up in the ladle was to be expected but the lead and tin contents were determined by analysis.

Two other similar series of ingots with lesser oxygen contents were taken, one after 2 hr. poling, and the third when the heat had been brought to pitch and was ready to pour. A list of these ingots, together with metallic additions, analyses and average test results is given in Table 1.

Disposition of Ingots

The ingots were sawed in two and a central slice $\frac{1}{4}$ in. thick cut from the center. One-half of each ingot was hot-rolled to 0.15 in. thick and, after annealing, was cold-rolled to 0.078 in. thick, a reduction of about 50 per cent. Lengths suitable for tensile test (2-in. gage length) were annealed in nitrogen for 1 hr. at 400° C., a temperature at which a high degree of ductility is normally developed in copper of moderate oxygen content. Ductility was measured as reduction of width at fracture, for reasons which have been discussed elsewhere.² From the other half of the ingot, millings were cut from the entire cross-section for chemical analysis. From the central slice a section for microscopic examination was cut, and a portion for conductivity measurement forged and cold drawn to 0.040-in. diameter wire. The resistivity at 20° C. was measured (Kelvin bridge) following annealing at 375° C.

Rolling Properties

Workability was qualitatively noted by observing the perfection of an initially smooth edge on the ingot, after it had been hot-rolled and cold-rolled to the finished size. The known effect of oxygen³ in progressively impairing the cold-rolling properties up to a limit of workability at about the eutectic concentration was observed. Lead and tin in the more highly oxidized coppers (above 0.1 per cent. oxygen) affected the rolling properties, both hot and cold, to no perceptible degree. At 0.04 per cent. oxygen, tin was found to have no effect, whereas lead in amounts greater than the oxygen content promoted a very slight roughening or checking of the edge during cold-rolling.

Effect of Lead and Tin on Conductivity and Tensile Properties

Detailed results of tensile and other tests are given in Table 1. In general, lead and tin up to 0.1 per cent. by analysis induce relatively minor effects on the several properties measured; in contrast, oxygen has a dominating influence such that, owing to unavoidable variations in oxygen content between the several ingots of a group, rather more attention has had to be given to the effects of oxygen than its triteness would at first seem to warrant. In order to isolate the effects of lead and tin from variations due to oxygen, the data of Table 1 have been recalculated, based on the indicated effect of oxygen for minimum amounts of other metals (Figs. 1, 4, 7), making due allowance for departures in oxygen content from three constant values of 0.04, 0.10 and 0.30 per cent. respectively. For example, the ductility of tests

² Pilling and Halliwell: *Proc. A. S. T. M.*; preprint, 1925.

³ Hanson, Marryat and Ford: *Jnl. Inst. Met.* (1923) **30**, 197; F. Johnson: *Metal Industry* (1925) **27**, 205.

from ingot 22 has been decreased by 0.2 owing to an oxygen content 0.009 per cent. below the standard value. These form the basis of Figs. 2, 3, 5, 6, 8 and 9.

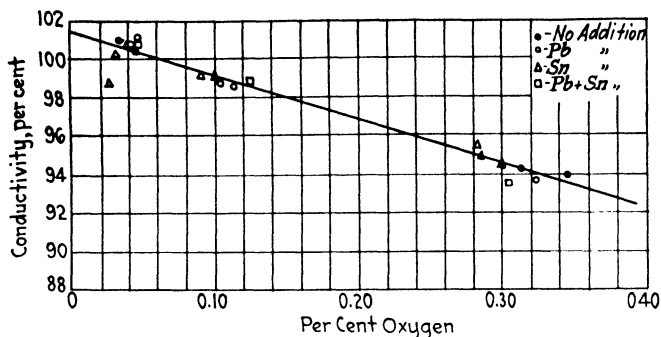


FIG. 1.—EFFECT OF OXYGEN ON CONDUCTIVITY OF COPPER.

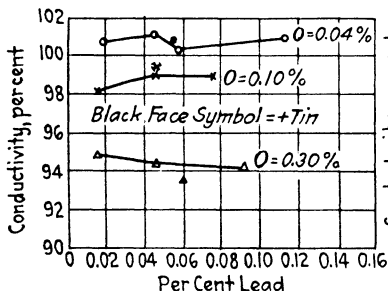


FIG. 2.—EFFECT OF LEAD ON CONDUCTIVITY OF COPPER.

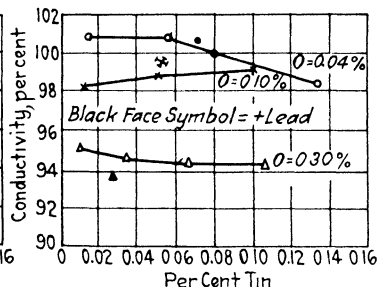


FIG. 3.—EFFECT OF TIN ON CONDUCTIVITY OF COPPER.

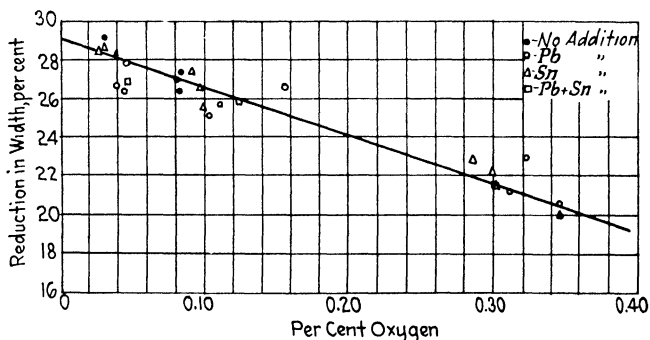


FIG. 4.—EFFECT OF OXYGEN ON DUCTILITY OF COPPER.

Effect of Oxygen

The effect of oxygen in the presence of lead and tin on conductivity, ductility and tensile strength is shown in Figs. 1, 4 and 7. In these curves the added metals are identified and the amount roughly indicated

by the notational scheme used. Oxygen decreases both conductivity and ductility, the effect of each 0.1 per cent. oxygen being to lower the

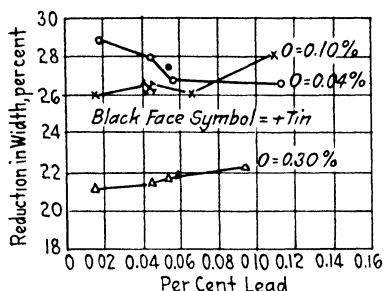


FIG. 5.—EFFECT OF LEAD ON DUCTILITY OF COPPER.

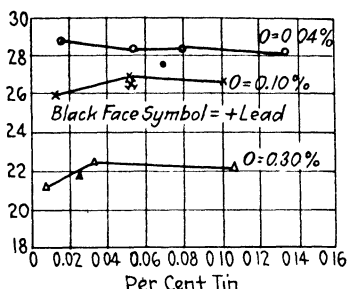


FIG. 6.—EFFECT OF TIN ON DUCTILITY OF COPPER.

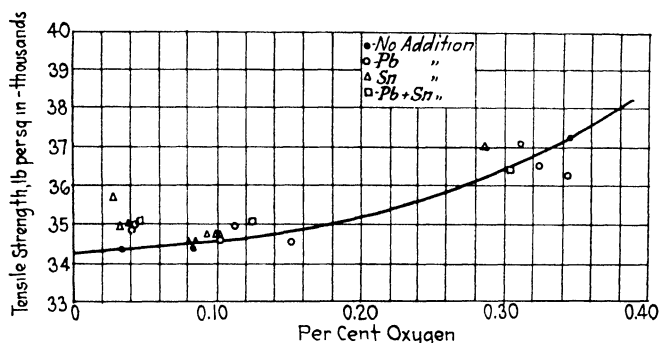


FIG. 7.—EFFECT OF OXYGEN ON TENSILE STRENGTH OF COPPER.

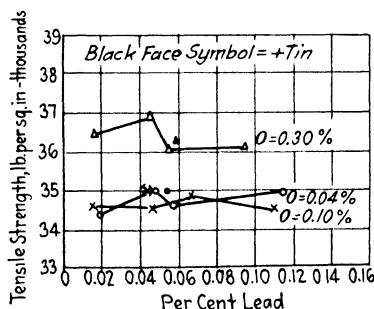


FIG. 8.—EFFECT OF LEAD ON TENSILE STRENGTH OF COPPER.

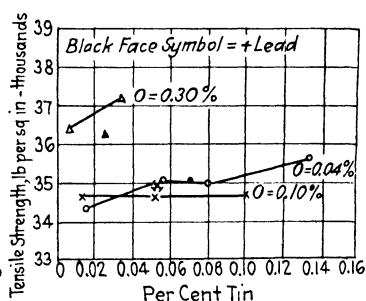


FIG. 9.—EFFECT OF TIN ON TENSILE STRENGTH OF COPPER.

former by 2.3 per cent., the latter by 9 per cent. of the maximum values. This quite overshadows any additional effect of either lead or tin. Tensile strength rises with increase of oxygen.

Effect of Lead

Lead is practically without effect on conductivity even in the presence of little oxygen. The effect on tensile strength is uncertain, but at any

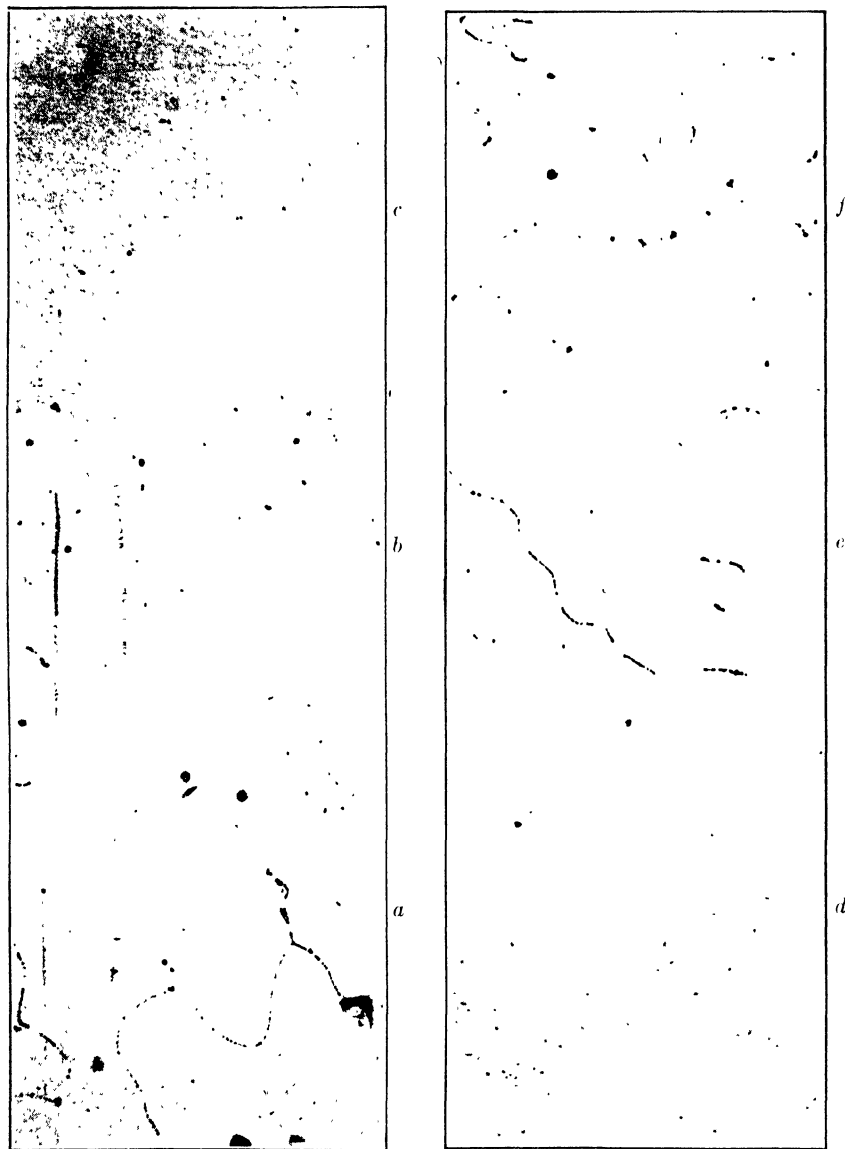


FIG. 10.—OXYGEN APPROXIMATELY 0.04 PER CENT. NOT ETCHED. $\times 100$. (a) Pb, 0.019; Sn, 0.016; (b) Pb, 0.018; Sn, 0.056. (c) Pb, 0.020; Sn, 0.080. (d) Pb, 0.021; Sn, 0.133. (e) Pb, 0.044; Sn, 0.016. (f) Pb, 0.057; Sn, 0.016.

event small. On the other hand, a definite increase in ductility is indicated when lead is added to an oxygen content of 0.1 per cent. or over.

With oxygen as low as 0.04, lead clearly diminishes the ductility. The presence of about 0.06 per cent. tin does not interfere with the effect of lead on low-oxygen copper; that is, strength and conductivity are unaffected, while ductility is reduced in accordance with the lead content.

Effect of Tin

The conductivity of high-oxygen copper is unaffected by tin up to 0.10 per cent. yet with oxygen at 0.04, tin beyond 0.06 causes a steady decrease in conductivity. This apparently means that not until this point is reached is tin present in metallic form to dissolve with the copper as a very dilute bronze, thus depressing the conductivity. Tensile strength is only slightly affected although a steady increase in strength with 0.04 per cent. oxygen may be noted. Amounts of tin even sufficient to decrease the conductivity are without effect on the ductility.

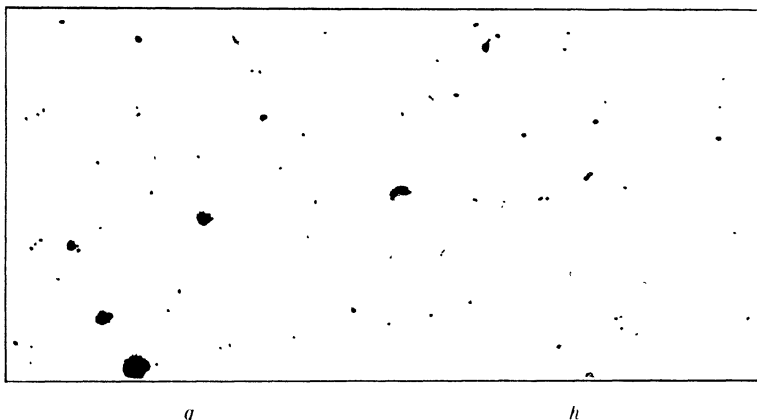


FIG. 10 (CONTINUED)—OXYGEN APPROXIMATELY 0.04 PER CENT. NOT ETCHED. $\times 100$. (g) Pb, 0.114; Sn, 0.016. (h) Pb, 0.053; Sn, 0.071.

In general, lead tends to reduce ductility, tin to reduce conductivity, but both of these tendencies are cancelled by oxygen in sufficient amount. Since one part oxygen by weight combines with 3.7 parts of tin to form SnO_2 it appears from the break in the conductivity curve at 0.06 per cent. tin that actually about 1.4 times the theoretically required oxygen content is needed to keep tin completely in the oxidized form, and that for similar reasons based on the subnormal ductility beyond 0.04 per cent. lead, this metal requires about 11 times the theoretical amount of oxygen. Although this estimate is only approximate, it is clear that tin is held in the oxidized form efficiently, whereas lead is not. The actual maximum tolerance might be expressed as a lead content equal to the oxygen content, or a tin content twice the oxygen content. Conservative practice would suggest a liberal factor of safety.

In all of the higher oxygen ingots, of groups 1 and 2, the margin of excess oxygen as thus defined is distinct.

Microstructure

It is evident from an inspection of the microstructures given in Fig. 10 that both lead and tin form oxide constituents which do not form a

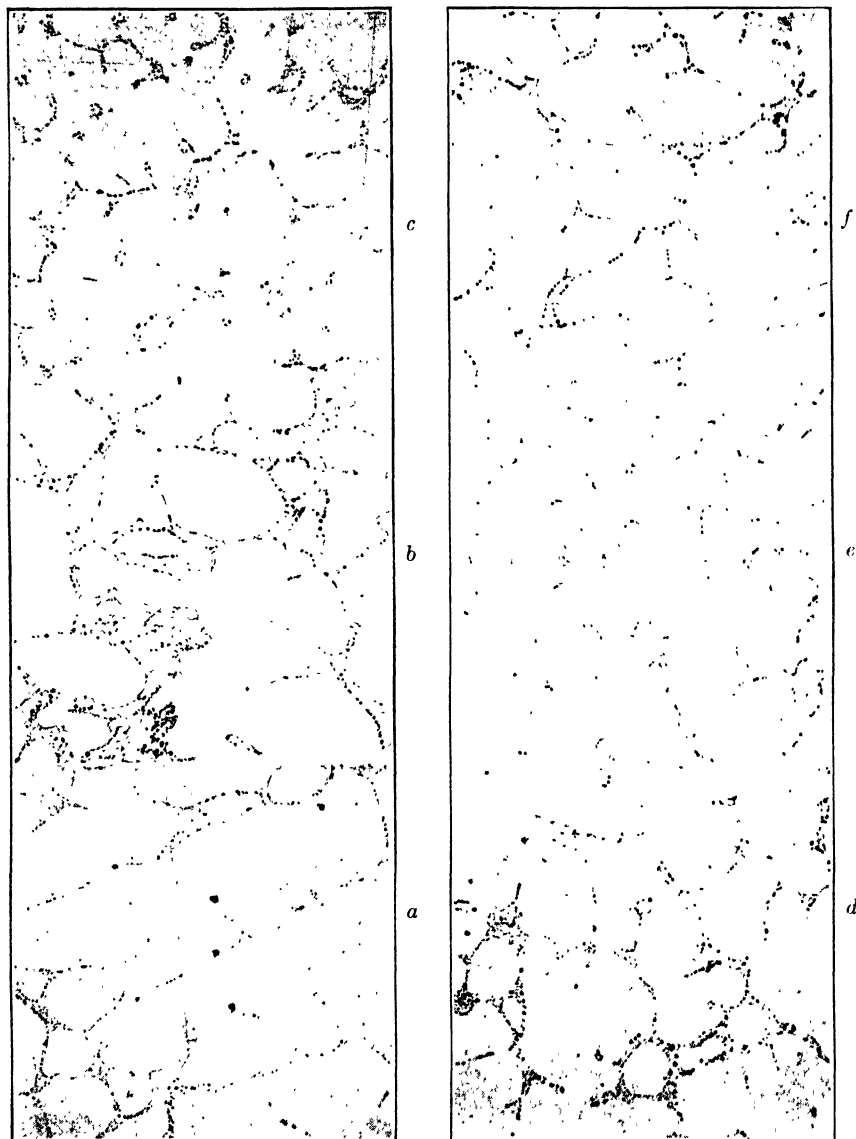


FIG. 11.—OXYGEN APPROXIMATELY 0.1 PER CENT. NOT ETCHED. $\times 100$. (a) Pb, 0.016; Sn, 0.012. (b) Pb, 0.017; Sn, 0.057. (c) Pb, 0.022; Sn, 0.101. (d) Pb, 0.020; Sn, 0.101. (e) Pb, 0.044; Sn, 0.018. (f) Pb, 0.067; Sn, 0.015.

eutectic with copper. In the presence of 0.03 to 0.05 per cent. oxygen, an increase in the tin content from 0.016 to 0.056 per cent. resulted in

the complete elimination of the oxide eutectic as a structural element, and still larger amounts of tin gave a greater dispersion to these oxide particles. Lead, on the other hand, while less powerful in destroying the eutectic, finally dispersed it completely; the oxide particles, although scattered, have coarsened, in contrast to the opposite effect of tin. With larger contents of oxygen (Figs. 11 and 12) these effects are far less clearly shown, yet a suggestion of the lead effect remains as the rather consistent occurrence of coarse oxide particles immediately enveloping the dendritic copper crystals in the more highly leaded ingots. The reduction in amount of eutectic is difficult to trace.

These effects are best seen in unworked ingot sections and are very largely lost when the metal is rolled, with the attendant mechanical

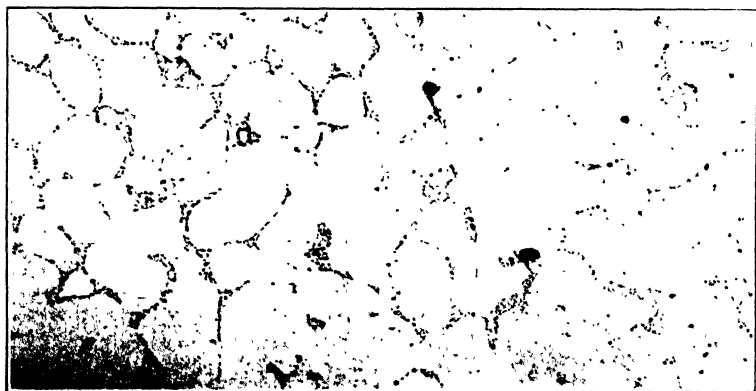


FIG. 11 (CONTINUED).—OXYGEN APPROXIMATELY 0.1 PER CENT. NOT ETCHED
× 100. (g) Pb, 0.110; Sn, 0.015. (h) Pb, 0.044; Sn, 0.053.

dispersal of the eutectic. Ingot 32 with a tin content sufficient to depress the conductivity appreciably showed no coring after etching.

RESIDUAL LEAD AND TIN

A careful distinction should be made between the effects of lead and tin added to copper of a given oxygen content, and residual amounts of these metals present in copper as it is brought to pitch in the furnace. To be of value, a close comparison of the effects of the presence of lead and tin in high-grade copper should preferably be made only with full-sized bars produced by large-scale operations, in order to minimize interference with the delicate conditions affecting the "pitch" of the heat. In order to approximate this, two groups of 225-lb. wirebars were chosen for test. The first group was composed of three electrolytic bars selected as representative from large stocks of a well known brand; it may be assumed that these bars, proved free from lead and tin, are

TABLE 1.—*Condensed Data*
Tensile Results are Averages of Three or More Tests

Group	Ingot Number	Ladle Additions, Grams				Chemical Analysis				Tensile Strength Lb./In. ²	Red. Width, Per Cent.	Elongation, Per Cent. in 2 In.	Conductivity, Per Cent.	Condition of Edge after Rolling	Micrograph Fig.
		Lead	Tin			Cu	O	Pb	Sn						
1	13					99.64	0.35	0.016	0.008	37,300	20.0	40.7	94.1	Rough, a few breaks; sheet split	12a
	14		2.3			99.68	0.28	0.020	0.033	37,000	22.9	40.1	95.2	Almost perfect.	b
	15		4.1			99.65	0.28	0.017	0.067	*	*	*	94.7	Rough and broken; sheet split	c
	16	2.3				99.63	0.35	0.054	0.009	36,300	20.5	39.4	94.2	Rough and slightly broken	f
	17	1.4				99.65	0.31	0.045	0.009	37,100	21.2	38.7	94.2	Rough and broken	e
	18	5.0				99.63	0.32	0.093	0.010	36,600	21.8	42.6	93.8	Rough and broken; sheet split	g
	19		5.9			99.59	0.30	0.019	0.106	34,200	22.2	33.7	94.5	Very rough and broken	d
	20	1.4	2.3			99.64	0.30	0.059	0.026	36,400	21.7	40.8	93.6	Rough and broken	h
2	21					99.88	0.082	0.016	0.012	34,600	26.5	48.0	98.7	Slightly rough	11a
	22		2.3			99.86	0.091	0.017	0.051	34,800	27.4	51.3	99.2	Slightly rough	b
	23		4.1			99.83	0.098	0.022	0.101	34,700	26.7	51.4	†	Almost perfect	c
	24		5.9			99.82	0.100	0.020	0.101	34,700	25.6	46.7	99.3	Slightly rough	d
	25	1.4				99.84	0.103	0.041	0.018	34,600	26.5	46.2	99.0	Somewhat rough	e
	26	2.3				99.83	0.113	0.067	0.015	35,000	25.8	46.4	98.7	Slightly rough, a few edge cracks	f
	27	5.0				99.77	0.156	0.110	0.015	34,500	26.9	48.1	98.7	Slightly rough	g
	28	1.4	2.3			99.81	0.124	0.044	0.053	35,100	25.9	47.8	99.1	Almost perfect	h
3	29					99.95	0.033	0.019	0.016	34,700	28.8	51.4	101.0	Perfect	10a
	30		2.3			99.92	0.040	0.018	0.056	35,100	28.3	47.8	100.8	Perfect	b
	31		4.1			99.90	0.031	0.020	0.080	34,900	28.6	53.2	100.2	Perfect	c
	32		5.9			99.85	0.028	0.021	0.133	35,700	28.4	46.0	98.8	Perfect	d
	33	1.4				99.92	0.047	0.044	0.016	35,000	27.8	45.1	101.1	Slightly rough	e
	34	2.3				99.89	0.044	0.057	0.016	34,860	26.6	49.7	100.5	Slightly rough	f
	35	5.0				99.86	0.041	0.114	0.016	35,000	26.7	48.6	101.0	Somewhat rough	g
	36	1.4	2.3			99.87	0.046	0.053	0.071	35,100	27.3	47.0	100.8	Rough	h

* Sheet too imperfect for test

† Wire not drawn

TABLE 2.—*Effect of Lead and Tin on Wirebar Copper*

Group	Kind	Wire-bar Number	Chemical Analysis							Electrical Properties		Tensile Properties ^a			Grain Size, Min.
			Cu	O	Pb	Sn	Fe	S	Si	Specific Resistance Microhm-cm at 20° C	Conductivity, Per Cent	Tensile Strength, Lb./In. ²	Red in Width, Per Cent	Elongation, Per Cent in 2 In.	
A	BER Electrolytic.	1	99.94	0.073	nil	nil	0.003	0.002	nil	1.711	100.8	32,400	26.5	49.2	0.036
		2	99.94	0.079	nil	nil	0.004	0.002	nil	1.732	99.6	32,500	26.4	50.3	0.039
		3	99.93	0.068	nil	nil	0.006	0.002	nil	1.725	99.9	32,600	26.5	48.5	0.035
B	Lead—Tin	4	99.94	0.057	0.010	0.015	0.005	0.004	nil	1.695	101.7	32,500	26.4	49.2	0.026
		5	99.93	0.060	0.010	0.015	0.005	0.002	nil	1.707	101.0	32,600	27.6	49.8	0.028
		6	99.92	0.068	0.012	0.019	0.004	0.002	nil	1.714	100.6	32,300	28.1	52.3	0.030
		7	99.92	0.071	0.009	0.020	0.005	0.002	nil	1.716	100.5	32,600	25.8	50.0	0.028
		8	99.91	0.065	0.010	0.019	0.005	0.002	nil	1.707	101.0	32,500	27.5	50.5	0.024
		9	99.91	0.070	0.010	0.019	0.004	0.002	nil	1.711	100.8	32,500	27.7	49.8	0.025

^a Three tests

fair samples of current electrolytic grade. For comparison, the second group was composed of six wirebars fire-refined from high-grade scrap copper containing solder. These bars were taken from a 25-ton heat

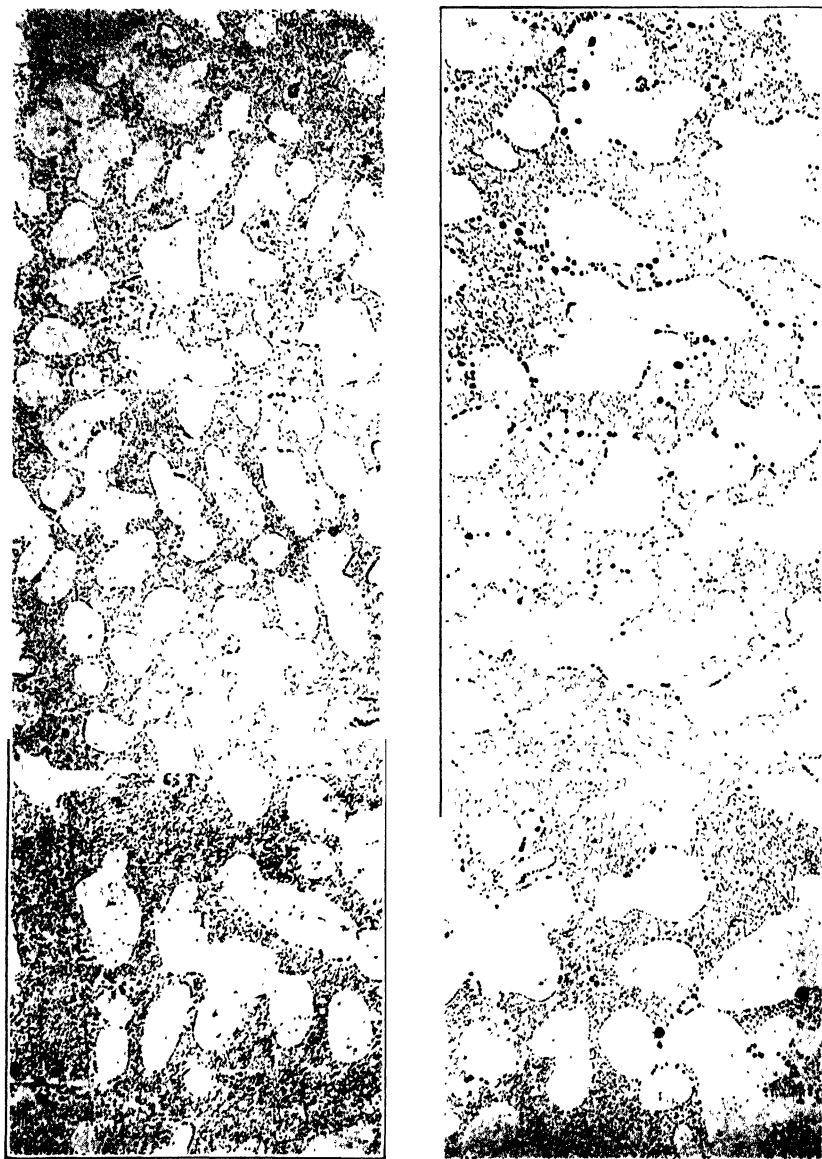


FIG. 12.—OXYGEN APPROXIMATELY 0.3 PER CENT. NOT ETCHED. $\times 100$. (a) Pb, 0.016; Sn, 0.008. (b) Pb, 0.020; Sn, 0.033. (c) Pb, 0.017; Sn, 0.067. (d), Pb, 0.019; Sn, 0.106. (e) Pb, 0.045; Sn, 0.009. (f) Pb, 0.054; Sn, 0.009.

refined and brought to pitch under commercial conditions with a total residual lead plus tin content of about 0.03 per cent. Judged by the

data developed in the first section of this paper, the oxygen content of the bars of this group afforded a factor of safety of about 3. All these bars hot-rolled and cold-rolled excellently.

All were rolled full size to strip 0.078 in. thick, the final cold reduction being 47 per cent. The final anneal was 1 hr. at 600° C. in nitrogen, and was under laboratory control. Conductivity was measured with wire drawn from a portion of hot-rolled bar to 0.040-in. diameter and annealed at 425° C. for 10 min. Chemical analyses were made on full section millings from hot mill crops.

The full experimental data are given in Table 2. Since the bars of each group ran rather consistently to type, it is convenient to compare the averages struck from each.

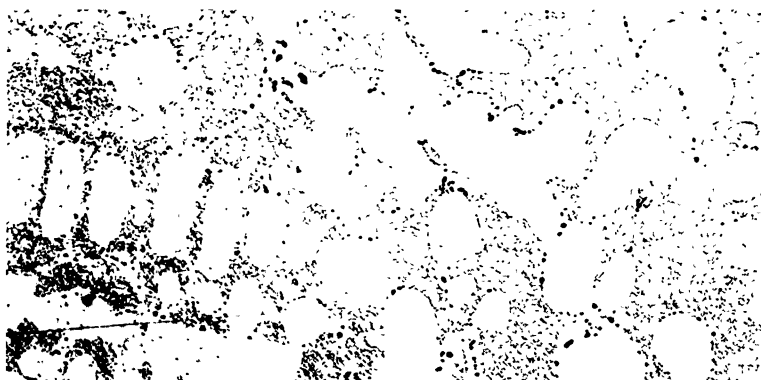


FIG. 12. (CONTINUED).—OXYGEN APPROXIMATELY 0.3 PER CENT. NOT ETCHED. $\times 100$. (g) Pb, 0.093; Sn, 0.010. (h) Pb, 0.059; Sn, 0.026.

TABLE 3.—Average Data

Group	Analysis				Cond Per Cent	Tensile Strength, Lb. In. ²	Red Width, Per Cent	Elong Per Cent 2 In.	Grain Size, Mm.
	Cu	O	Pb	Sn					
Electrolytic	99.94	0.073	nil	nil	100.1	32,500	26.5	49.3	0.038
Lead-tin	99.92	0.065	0.010	0.018	100.9	32,500	27.2	50.3	0.027

Although the electrolytic bars averaged higher in copper content, the lead-tin bars are, by a small but consistent margin, both more ductile and of higher conductivity. The better ductility of the lead-tin bars is only partly accounted for by their lower oxygen content and may be largely due to their finer grain size,⁴ a feature which has been rather consistently noted. The conductivity difference is more striking in that the average electrolytic value is below the lowest lead-tin, and is too great to be

⁴ Pilling and Halliwell: *Op. cit.*

accounted for by the difference in oxygen content. The lower strength of the copper in these two groups, as compared with the tests in Table 1, is fully accounted for by the difference in annealing temperature.

It is clear, therefore, that residual lead and tin may be present to a total of a few hundredths per cent. in wirebar copper without loss of either ductility or conductivity.

CONCLUSIONS

1. Tin and lead may be present in copper of commercial purity without loss of either ductility or conductivity provided the sum of the lead and half the tin contents does not exceed the oxygen content. This may be regarded as the maximum tolerance, not to be approached in conservative practice.

2. When the above condition is observed, the tensile and electrical properties of copper containing lead and tin are directly related to the total oxygen content.

3. When the above condition as to oxygen content is not observed, an excess of tin depresses the conductivity and is without effect on the ductility; an excess of lead reduces the ductility without appreciable effect on the conductivity, and impairs the cold-rolling properties.

4. A careful comparison of wirebars produced under commercial conditions has shown that copper containing residual lead and tin up to 0.03 per cent. total is fully the equal, both as to conductivity and ductility, of average grade electrolytic wirebars.

ACKNOWLEDGMENT

Acknowledgment is made of the helpful cooperation of Mr. H. F. Seifert in permitting use of the reverberatory refining furnace, of Mr. C. R. Stevens in supervising the rolling of the ingots, and to Mr. S. M. Kintner, Manager, Research Dept., of the Westinghouse Co., for permission to publish these results.

DISCUSSION

S. SKOWRONSKI, Perth Amboy, N. J.—It must be rather startling to the copper refiner to find that lead does not have much effect upon the rolling quality of the copper, and the conclusions of Messrs. Pilling and Halliwell must be carefully interpreted in order to avoid any misconception.

In the rolling of copper into sheets, starting with the usual copper cake, or wedge bar, lead is a very deleterious element, and there is positive evidence that copper containing as low as 0.0075 per cent. of lead will fail on rolling, the copper being hot short giving serrated edges to the copper sheet. This with the normal amount of oxygen to be found in refined copper 0.03 to 0.04 per cent.

The manner in which the copper is rolled whether in closed or open passes undoubtedly has an influence on the amount of lead which may be allowed in the copper, and under the authors' condition, a much higher lead content is permissible.

The authors are correct when they state that lead has no effect upon the electrical conductivity of copper. Experimentally it has been found that copper containing as much as 0.5 per cent. of lead has the same conductivity as the original copper without the addition of lead.

In fact lead will increase the conductivity of copper, where the decrease in conductivity is due to the presence of arsenic. For example copper containing 0.0104 per cent. of arsenic with a conductivity of 97.3 can have its conductivity increased to 100.2 per cent. by the addition of 0.12 per cent. of lead.

W. H. BASSETT, Waterbury, Conn.—The reason why we advocate a lead limit of 0.005 per cent. is because when cake copper is hot-rolled to sheets, edge cracks begin to be noticed with lead at 0.005 per cent., and with more lead, the cracks become worse.

It makes much difference whether one is rolling copper or just "playing" with it. If one is willing to put it through the rolls, back and forth, almost an unlimited number of times, to reduce it a certain amount, more lead can be tolerated than if it is pinched to the full capacity of the rolls. The modern practice of rolling copper is to squeeze as much as the rolls will stand. Certainly copper, if it is well refined, will not stand a lead impurity. Tin does not affect to any extent the ductility of copper. Copper can be rolled with tin in it up to 2 per cent.—I am now speaking of hot-rolling. Using care, copper can be cold-rolled with lead in it up to 1 per cent. In cold-rolled copper small amounts of lead do not seriously impair the ductility.

The authors quote Mr. Addicks in regard to overpoling: "The unstable condition can be controlled by adding certain substances, notably lead, in small quantities, but as mere traces of lead make copper brittle, the cure is worse than the disease." Overpoled copper usually contains oxygen in considerable amounts. The authors have not taken into consideration the sulfur that is contained in overpoled copper.

Of course, the relative amounts of oxygen and lead present must be taken into consideration. There is no doubt that tin oxide can occur in copper if it contains considerable oxygen. We have found that when this condition exists, solution of the copper in nitric acid leaves grains of tin oxide, beside the usual precipitate of metastannic acid.

The other impurities in the copper were not taken into consideration by the authors. The samples should have been subjected to complete analysis. In considering grain size, the question of the effect of impurities other than lead and tin were not taken into consideration. Of course, tin raises the annealing temperature of copper, and to make a proper com-

parison the material should have been annealed to the same grain size instead of the same temperature. The conductivity in Table 3 of average data shows electrolytic copper to have a conductivity of 100.1, and copper containing the lead and tin to have a conductivity of 100.9. An electrolytic copper may contain silver, which would have little effect on conductivity, but would have a very decided effect on annealing temperature and grain size. It may contain nickel, which will decrease the conductivity more than either tin or lead, lead having practically no effect and tin having but small effect. It may contain arsenic, which would not make very much difference to grain size, in the small amounts which could be present and have the conductivity given. We really do not know what there was in the electrolytic copper to reduce its conductivity, and the copper which contained lead and tin may have been of very high purity, except for the lead and tin.

The refining which this copper has received may have removed some of the impurities which the electrolytic copper originally contained.

Of course, we cannot agree with the authors' conclusion: "Tin and lead may be present in copper of commercial purity, without loss of either ductility or conductivity provided the sum of lead and half the tin contents does not exceed the oxygen contents. This may be regarded as the maximum tolerance, not to be approached in conservative practice."

Suppose in commercial copper we have 0.02 per cent. of oxygen present, and then we might have lead under those conditions present as 0.015 per cent., and tin as 0.010 per cent. The tin would not affect the ductility, and the lead would be extremely disastrous in hot-rolling. Of course, there is a relation between the amount of lead that copper will carry, and oxygen, but copper which is proper for use in the arts, must have low oxygen. Oxygen approaching 0.1 per cent., has a considerable effect on the ductility of copper. Formerly, this might have been tolerated in copper sheets for roofing, where the copper was not mechanically worked to any extent, but if the oxygen approaches 0.1 per cent., the ductility of copper, and its fatigue resistance, we believe, is reduced considerably. Under modern conditions, in the use of copper, those points must be observed.

In the third paragraph the authors say that lead reduces the ductility, without appreciable effect on conductivity, and impairs cold-rolling properties. It impairs hot-rolling properties, but once the copper is broken down, you can cold-roll it practically as much as if there were not any lead present.

So I think that while this paper is a good exposition of the fact of the counteracting effect of oxygen on the influence of lead in copper, particularly in the hot-working of copper, it would lead to many wrong conclusions if we took it without some further consideration of the matters which I have just talked about.

C. S. WITHERELL, New York, N. Y.—I would like to ask the authors, when they speak of percentage of oxygen in copper, whether they refer to the total oxygen or what is nowadays, I think, called optical oxygen, which means that oxygen which can be accounted for by the oxygen constituent visible under the microscope, whether a suboxide or a eutectic composed of suboxide with copper?

N. B. PILLING.—The oxygen given is that which was determined by direct chemical analysis.

C. S. WITHERELL.—After the oxidizable impurities have been satisfied, to the extent possible, then any more oxygen present must be there combined with copper and be visible under the microscope as the oxygen constituent. It is obvious that impurities are much less harmful if in the form of oxides and merely held in suspension than if they were in the elemental state alloyed with the copper. To insure this condition enough oxygen-constituent (considered to be suboxide of copper) must be present; however, as is well known, too much oxygen-constituent must be avoided, whether the impurities be present or not. There is a rather delicate balance, hence it is probably more important to have some criterion of that oxygen appearing in combination with copper than to know the total oxygen present. There is no better criterion than that indicated by the microscope, which not only shows to what extent the copper oxide has been formed but also how segregated and whether or not the impurities which form solid oxides have, to a large extent, been put into that condition.

F. R. PYNE, Perth Amboy, N. J.—Weight must be given, as Mr. Bassett has said, to the other traces of impurities in the copper. In some of these papers, that has too frequently not been given sufficient weight.

C. R. HAYWARD, Cambridge, Mass.—I wish to object, on theoretical grounds at least, to any statement that the presence of any impurity does not affect the conductivity of copper. For practical purposes, we may put up with small quantities of various impurities, but I feel sure that the copper metallurgists should not rest satisfied until they have produced the purest possible copper, as free as possible from impurities, either dissolved or free, and also as free as possible from voids. When such a copper is produced, it will have properties far superior in many respects to the best commercial grades today.

The recently published tests on a single crystal of copper, that have been made in the laboratories of the General Electric Co., have been extremely interesting, and show some of the intrinsic properties of pure copper. How nearly we can ever approach to those properties, at least, so far as conductivity is concerned, it is impossible to say, but we have been too much accustomed to consider copper containing oxygen, even

though quite free from other impurities, as the best copper that can be produced.

Even these small traces of oxygen, admitting perhaps that it is difficult to measure their effect as far as conductivity is concerned, must have some effect on conductivity, and several times today it has been pointed out that traces of one thing or another undoubtedly lower the conductivity of the copper and affect its resistance to fatigue failure and its behavior in working.

We also forget that there is often a change in the composition of copper, as it flows from the furnace to the mold and during setting. Most of our practical copper metallurgists minimize the absorption of oxygen during this period but I have made tests which show that the absorption is considerable, and I feel confident that it has a bad effect upon the final properties of the copper as the fabricator has to receive it.

I merely wish to make a plea for a continued effort toward getting, shall I say, a chemically pure copper; and when that day comes, we will, I believe, look back upon our present complacency with shame.

W. C. SMITH, Baltimore, Md.—The question was asked whether the oxygen had been determined microscopically, optically or chemically. With lead and tin present, the microscopic oxygen is not much good; in fact, it is very erroneous.

C. R. STEVENS, East Pittsburgh, Pa.—I would regret very much to have the impression created that the authors desire to go on record as stating that lead and tin as impurities in copper are of no consequence or significance. They have proved in their paper that small quantities of lead and of tin with proportionate amounts of oxygen have no detrimental effects whatsoever on the ductility and the conductivity of commercially pure copper.

Ten years ago, I was confronted with the problem of using copper from which lead and tin could not be entirely eliminated. The copper to which reference is made is wirebars made from refined copper scrap containing small quantities of soldered leads, connectors, etc. Practical mill-working of the copper, based on fore-knowledge of its content, demonstrated that it possessed slightly greater ductility and conductivity than the average American electrolytic wirebar stock. The results obtained in the mill prompted us to make a thorough research test to determine the limits to which lead or tin or both could be present without detrimental results of copper. The paper presented by Dr. Pilling and Mr. Halliwell gives the results obtained in detail.

I attribute the successful working of lead- and tin-bearing copper to our refining and manufacturing processes. In our refining process, we oxidize the copper quite extensively, skim off the slag very carefully, cover the charge well, and reduce to the proper pitch. The oxidizing section of

the refining process is carried beyond the stage of the disappearance of metallic lead which is determined by the disappearance of the lead line in the spectrocope. The elimination of lead is substantiated by chemical analysis made at the time. In the hot-rolling process, our equipment is such that the metal is worked on all four sides at once, thus giving equal distribution of pressure throughout the bar. This hot-rolling treatment builds up a grain structure at the beginning that is an insurance against edge fractures.

The wirebars we make from refined copper scrap have an extremely fine "set." The wrinkles are very small and indicate the absence of insoluble gases. The "set" surface has been milled from hundreds of bars and no cavities have been found.

The statement that lead present in copper is detrimental to making sheets does not necessarily prove that lead in very small quantities is the cause of cracked edges. Our research work and practical experience have demonstrated otherwise. We have made exhaustive comparative tests for edgewise ductility performance and have found that lead-and tin-bearing copper up to 0.03 per cent. of lead and tin showed a lower percentage for breakage loss than average electrolytic copper.

The ductility requirements for copper to bend edgewise around a pin are very high. As an example of the requirements, let me illustrate a standard operation in coil forming: Copper strap 0.045 by 0.625 in. is bent around a pin of $\frac{1}{2}$ in. diameter to an angle of 180° . The extreme outside edge stretches nearly 95 per cent. Of course, the compressive stresses acting on the inside edge compensate to some extent for the great elongation of the outer edge.

Another feature peculiar to refined copper bearing 0.03 per cent. lead and tin or less is the remarkable freedom of the metal from slivers and other surface defects. This feature is of great value when applied to the manufacture of large cross-section shapes such as rounds, squares, rectangles, wedges, etc. In closing, allow me to say that in 10 years' experience of manufacturing copper, during which period approximately 60,000,000 lb. of scrap copper has been refined, we have found the metal to be second to none for those qualities of prime importance to the electrical industry, viz., ductility and conductivity.

N. B. PILLING (reply to discussion).—Both Mr. Bassett and Mr. Skowronski have stressed the importance of lead on the ability of copper to hot roll without cracking. As they have suggested, the lead tolerance in rolling sheet from cakes may possibly be lower than in rolling narrower sections from wirebar where a considerable side support is given during the reduction. They are probably right in their contention that with heavy mill reductions lead, when present in amount sufficient to cause damage, has its principal effect in the hot- rather than the cold-

rolling properties. Our data on extremely high lead contents in experimental ingots do not afford a clear answer to this point.

As to the critical relation between the oxygen and the combined lead and tin contents, which forms one of the principal conclusions of the paper, Mr. Bassett does not seem inclined to agree, yet in the example which he cites as disproof, one finds reference only to hot-rolling quality and not to either cold-ductility or conductivity, regarding which the point in question is framed. We would also call attention to the fact that Conclusion 1, to which he objects, contains two sentences, only the first of which he has considered. We of course do not know and have not attempted to determine to what extent this critical ratio changes as the oxygen content is varied, but consideration of Ingot 27 in Table 1 would suggest that a considerable increase in the oxygen content from 0.04 to 0.15 per cent. does not diminish it to any great extent. We may therefore assume no important change in the range 0.02 to 0.06 per cent. oxygen. Although Mr. Bassett speaks of an oxygen: lead ratio of 4 to 1 and Mr. Skowronski implies that 5 to 1 is not enough, we have seen many wirebars of the lead-tin type of Table 3 in which (assuming that the small tin content accounts for a fraction of the oxygen content in accordance with Conclusion 1) the oxygen: lead ratio is about 3 to 1, hot rolled and cold rolled on a commercial scale to thin strap sizes with much success. Over 50,000,000 lb. of copper of this type has been successfully worked by the Westinghouse company.

The quotation from Mr. Addicks regarding the evil effects of lead in copper, while made by us only to indicate the divergence of opinion indicated in the literature, we feel is distinctly misleading in the categorical and unqualified form in which it originally occurred.

Both Mr. Bassett and Mr. Pyne suggest that the two grades of copper compared in Table 2 may have differed in important respects as to the content of minor impurities other than the six for which analysis was made. We would not suspect great divergence in composition as the fire-refined heats were worked up initially from electrolytic scrap reverts, but admit the pertinence of the question. Mr. Bassett has agreed to make a careful analytical comparison between representative bars of these two groups, and the results he obtains from material now in his hands will be of value.

In principle, at least, we find no difficulty in agreeing with the remarks of Mr. Witherell regarding the importance of the form in which impurities are present, whether oxidized and precipitated, or in the reduced condition. This point received some attention in the paper by way of micrographs showing the oxide structures encountered; yet we have had some trouble in identifying with any certainty the minute quantities of these present in impure low-oxygen copper, not to speak of the difficulty of attempting a quantitative estimate of them.

It is perhaps only fair to state that our intention in presenting this paper was not to suggest any relaxation from the present standards of purity of refined copper, but by calling attention to the highly successful industrial use, in an application in which the physical and electrical requirements are severe, of copper containing an element commonly regarded as detrimental, to indicate what seems to be a lag between the literature of the art and its practice.

W. H. BASSETT (written discussion).—Samples of wire bar copper from Grades A and B, Table 2,⁵ were handed me by Messrs. Pilling and Halliwell for complete analysis in order, if possible, to obtain further information as to the reason for the difference in conductivity between these two grades. The result of this analysis follows:

Bar No	7	3
Brand	Lead-tin	B. E. R.
Conductivity	Per Cent. 100 5	Per Cent. 99 8
Copper	99 901	99 942
Silver	0 034	.0026
Arsenic0006	.0009
Antimony0013	.0011
Lead0093	.0004
Tin0163	.0000
Iron0051	.0020
Nickel0039	.0016
Selenium0005	.0006
Tellurium0007	.0007
Bismuth00003	.00005
Zinc0019	.0000
Sulfur0022	.0031
Oxygen060	.062

The composition gives no evident indication as to the reason for the high conductivity of the lead-tin copper as compared with the B. E. R. electrolytic sample. It is well known that lead and tin in small amounts have but little effect on conductivity, but with lead, tin, iron, nickel and zinc all higher in the lead-tin samples it is very difficult to understand why the conductivity should also be higher. Oxygen does not affect conductivity very rapidly and the oxygen in the electrolytic sample is only slightly above that in the lead-tin sample.

The heating, rolling and drawing of the wire, and also the annealing of these samples, was done at the same time and under exactly the same conditions. The microstructure is very similar.

⁵ See Table 2, page 689.

Exudations on Copper Castings

By W. H. BASSETT* AND J. C. BRADLEY,† WATERBURY, CONN.

(New York Meeting, February, 1926)

Beads of metal frequently appear at the ends of cast-copper wire bars and on the sides of wedge cakes near the top. These are richer in cuprous-oxide than the rest of the casting. A micrographical study of these exudations has been made. It is suggested that the material is forced through the surface while the copper is solidifying. If not eliminated in process of manufacture, it shows on the finished polished sheet copper in patches differing in color from the main body of the sheet.

FIGURES 1 to 4 show the copper exudations, at different magnifications, as they appear on the ends of cast wire bars, and on the sides, usually near the top, of wedge cakes. Sometimes the exudations are in fine "drops;" at other times, large masses of the material are found.

Microscopic examination of the copper exudation indicates that it is high in oxide and of eutectic proportions. Because of the difficulty of securing a suitable sample, the protuberances have not been analyzed chemically; but the spectroscope shows no indication that there are any more metallic impurities present than in the balance of the copper. The lowest copper plus silver content of the coppers studied for this paper was 99.914 per cent.; the highest, 99.966 per cent.; so the oxygen content of the whole casting would be well under 0.07 per cent.

STRUCTURE OF PROTUBERANCES

The segregation of oxide between grains in the interior of the cast bar, not far from the "set," is shown in Figs. 5 and 6. In general, the amount of cuprous oxide begins to increase at a point about 0.01 in. below the normal surface of the casting, *i. e.*, the base of the drop; but it does not attain maximum concentration in the main body of the metal.

Vertical sections, Figs. 7 to 12, show that there is a definite line of large cuprous-oxide globules at the base of the drops. Horizontal sections at this place show that these large globules lie in a thin billowy

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† The American Brass Co.

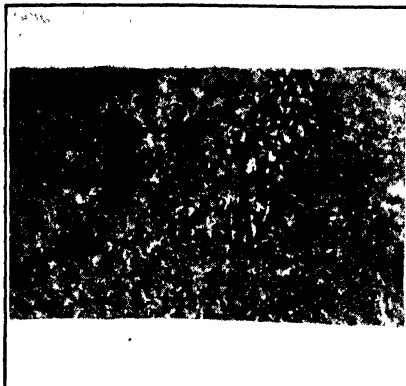


FIG. 1.— $\times 1$.

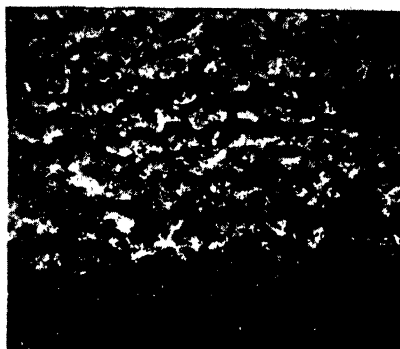


FIG. 2.— $\times 1.3$.

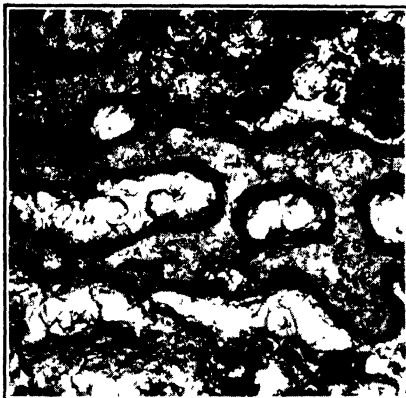


FIG. 3 — $\times 5$.



FIG. 4.— $\times 20$.

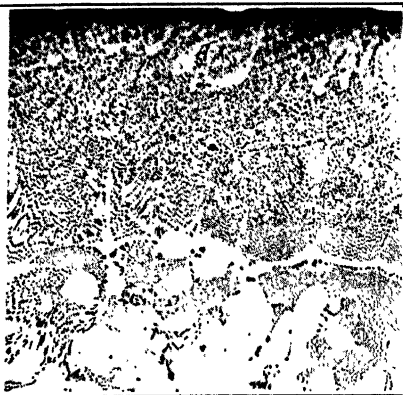
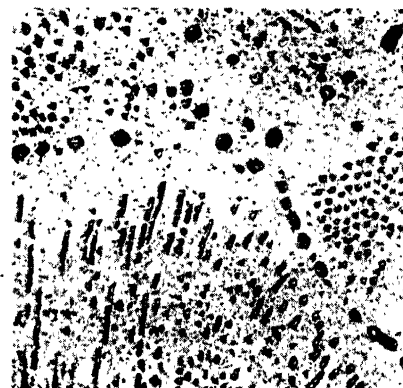
EXUDATIONS AS THEY APPEAR ON COPPER CASTINGS.



FIG. 5.—OXIDE SEGREGATION BETWEEN GRAINS OF COPPER CASTING; SECTION PARALLEL TO SET. $\times 75$.



FIG. 6.—OXIDE SEGREGATION BETWEEN GRAINS OF COPPER C SECTION PERPENDICULAR $\times 75$.

FIG. 7.— $\times 75$.FIG. 8.— $\times 75$.FIG. 9.— $\times 75$.FIG. 10.— $\times 75$.FIG. 11.— $\times 100$.FIG. 12.— $\times 500$.

VERTICAL SECTIONS THROUGH EXUDATIONS ON COPPER CASTINGS.



FIG. 13.— $\times 75$.

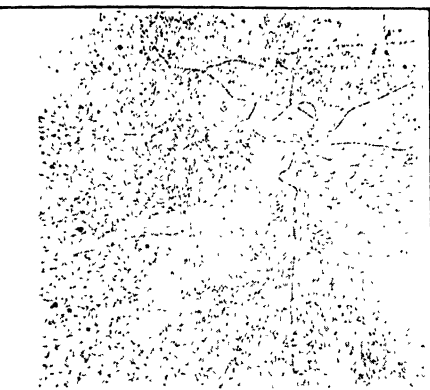


FIG. 14.— $\times 75$.



FIG. 15.— $\times 75$.



FIG. 16.— $\times 100$.

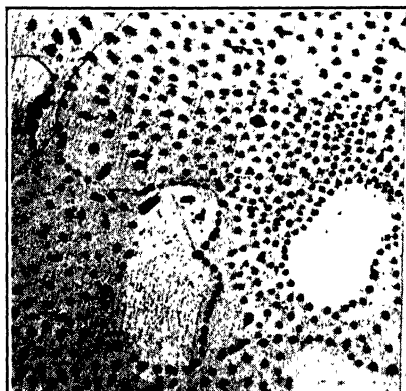


FIG. 17.— $\times 250$.

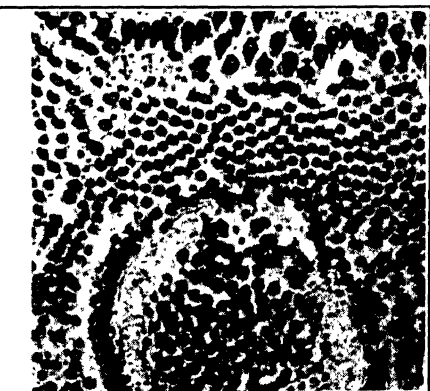
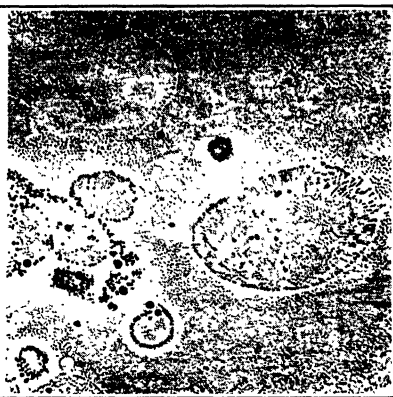


FIG. 18.— $\times 500$.

HORIZONTAL SECTIONS THROUGH EXUDATIONS ON COPPER CASTINGS.

sheet, one globule deep, across the whole basal portion. This phenomenon is brought out more distinctly by the single narrow band, free from cuprous oxide, lying adjacent. Beyond this clear narrow band the entire body of the drops is made up of a rich mixture of cuprous oxide in copper, broken only by distinct lines of oxide globules resembling those of the crystal boundaries within the casting proper. These division lines occur only in the larger drops and suggest that the metal forming the drops flowed from more than one outlet and joined in a common mass. Half of such a drop is shown in Fig. 10; another part, in Fig. 9. Where the drops are attached to the surface of the main body of the copper, the cuprous oxide globules are elongated in a direction nearly normal to the surface. Elongation of the cuprous oxide is also noticeable in the metal

FIG. 19.— $\times 75$.FIG. 20.— $\times 75$.

HORIZONTAL SECTIONS THROUGH EXUDATIONS ON COPPER CASTINGS.

underneath the drops. There appear to be no definite craters or channels from which the high cuprous oxide material exudes, but there is at least a well-defined structure to show general movement, or increase in oxide toward the drop. Figs. 13 to 20 show horizontal sections.

MECHANISM OF EXUDATION

Pure copper solidifies at $1083^{\circ}\text{C}.$; the eutectic material, carrying 0.39 per cent. oxygen, remains liquid until the temperature goes down to $1065^{\circ}\text{C}.$ ¹ As the copper of highest purity crystallizes, a gradual rise of oxygen-rich mother liquor occurs in the mold, as evidenced by the concentration of cuprous oxide being greater near the top of the casting and in the set than in any other part. It is such material as this of eutectic proportions that constitutes the protuberances. At first, while most

¹ Heyn: Equilibrium Diagram. Z. Anorg. Chem. (1904) **39**, 1.

Desch: Metallography. (1913), 205.

of the copper is molten, the hydrostatic pressure makes the solid envelope of the casting hug the mold. Soon contraction, the result of cooling, leaves a space between the mold and the copper; into this is forced some of the copper-cuprous oxide eutectic, which has been entrapped between crystals of purer copper, forming the exudations at the sides near the top of the cake or bar.

EFFECT OF EXUDATIONS ON ROLLED COPPER

When wedge cakes and other shapes are so rolled that the surfaces carrying exudations correspond with the finished surfaces of the sheet metal, these high oxide areas will sometimes appear in patches differing

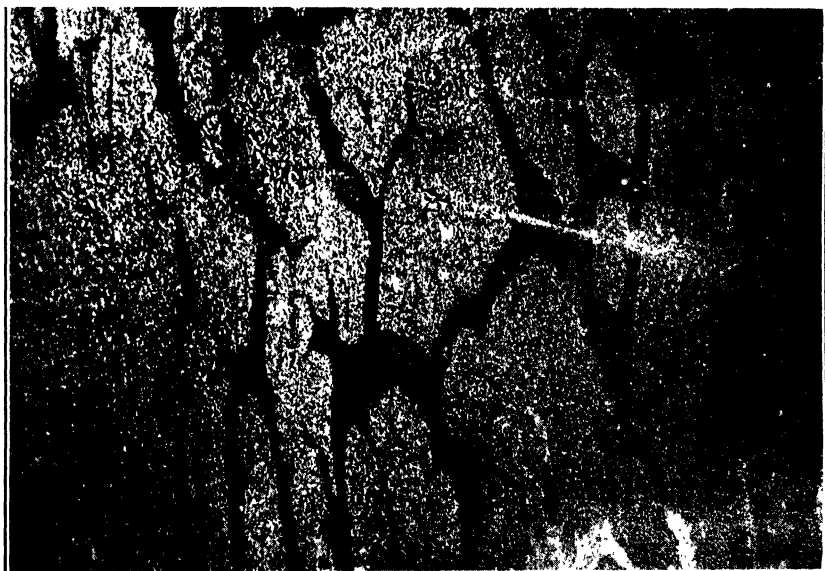


FIG. 21.—BROWN STAIN ON POLISHED SHEET RESULTING FROM EXUDATIONS ON COPPER CASTINGS; HEAT TINTED. $\times 1$.

in color from the rest of the sheet. If the metal is highly polished and held in the proper light, these spots look brown in contrast with the clean copper. The spots vary in shape; some are streaked, some form in a lacey pattern, others look like leopard spots. The spots change shape on polishing deeply. The shape depends on the way the protuberances occur in casting and on the direction in which the metal is rolled. Fig. 21 illustrates these spots, the sample having been prepared by heating, to bring out the color contrast.

If in process of manufacture the surface is heavily "scaled," or scalped so the protuberances are removed, the brown stains do not appear.

DISCUSSION

F. R. PYNE, Perth Amboy, N. J.—Exudations are always on the ends of the wire bars or on the upper part of the cake. That is where the mold is thinnest, and the copper gets its first cooling.

Mr. Bassett's analysis—that the copper oxide released by the release of pressure through the shrinkage of the solid metal in the mold—is probably correct. It is very difficult to prevent exudation, except by using very thick molds and keeping them hot. Exudation occurs in the early part of the casting more than later when the mold is hot.

H. A. SHAW, Seymour, Conn.—Is it not a poor condition in the mold that is largely responsible for the formation of exudations?

C. S. WITHERELL, New York, N. Y.—It is very pronounced on the broad flat ends of blunt-end wire bars. It is the end of the bar that draws away from the mold very quickly, and at that time it is just below the freezing temperature of copper and since the bar is shrinking it is understandable that any liquid constituent would squirt out through whatever surface pores it may find.

I do not know what we can do about it, except to regulate the temperature of the molds, and we have so many other things to regulate in casting wire bars that I do not think we want to load any others on ourselves. However, if the molds are properly proportioned for uniform cooling and are at the right temperature for pouring, the trouble seems to disappear.

W. H. BASSETT.—In making polished copper there are so-called ghost marks, lace patterns, etc., on the surface of the copper which are caused by a slight difference in color between the pure copper and the copper oxide eutectic. Such pattern is observed where these exudations are rolled in.

C. S. WITHERELL.—It seems to me that the value of such rolled copper would be sufficient to warrant the expense of scalping the copper before rolling it. It is a very simple means of removal. On all other copper you would not care whether the markings were there or not.

H. A. SHAW.—It is customary on certain kinds of copper to scalp to the extent of 5 per cent. on the surface, and even that does not take it out on both surfaces on the wedge cake.

C. S. WITHERELL.—That would be about $\frac{1}{4}$ in. ($\frac{1}{8}$ in. per side) on a 5 or 6-in. cake.

H. A. SHAW.—That is after it is rolled.

C. S. WITHERELL.—That is about $\frac{1}{8}$ in.

Microscopic Structure of Copper

BY H. B. PULSIFER, CLEVELAND, OHIO

(New York Meeting, February, 1926)

THE following report on the structure of copper is the result of work done in the laboratory of the Rome Wire Co. early in 1925. Previous work had indicated to the author that excellent results might be expected if a suitable technique in surfacing and etching could be developed. The resources of the Rome Wire Co. enabled this metal to be studied more intensively than previously, although none of the materials were investigated exhaustively. The material presented is hardly more than a preliminary summary of the most obvious character of the metal; a much longer research would have been necessary to solve many of the pressing problems connected with the casting and working of copper.

The Rome Wire Co. has generously released the paper; to Dr. E. H. Darby, technical supervisor of the company, are due particular thanks for his appreciation of the importance of metallographic study of copper and for his effective support in the prosecution of the work and in making its publication possible.

DENDRITES, CELLS AND GRANULES

The microscope reveals at least three orders of structural units in copper, as in other metals. The largest structural units are the *dendrites*—spine-shaped crystals building up the masses of metal when it solidifies from a melt or is crystallized from solutions by chemicals or electricity. The *nucleus cells*, commonly called “grains,” are the largest and most conspicuous units of recrystallized solid metal; the limitations of their growth usually confine their sizes to microscopic proportions, although in “single crystals” they may become as large as the piece of metal itself. The *granules* are the microscopic fine-structural blocks or laminations that build up the nucleus cells; they are revealed when metal is etched with suitable chemicals. The granules are commonly visible at 500 diameters magnification and are plainly visible at 1000 diameters; magnification of the granular surfaces up to 6000 to 9000 diameters shows no finer units, not because of lack of optical resolution but because the chemical attack has left an unfeathered smooth surface.

absence of very pronounced borders, one is not certain whether all the parts belong to one dendrite or to several. Several blunt ends and continuous metal from one division to another indicate that most of the lines may be partitions in the same crystal instead of borders between dendrites. The vugs, rows of globules, and inclusions along the division



FIG. 3.—SUTURE LINES IN A DENDRITE; ETCHED WITH AMMONIACAL PEROXIDE. $\times 700$.

lines are not as pronounced as may be found in wire-bar sections; this print likewise does not show metal as clean and massive as it frequently occurs and is always desired in wire bars.

A more intimate view of suture lines is given in Fig. 3, where the fineness of the division lines, the quality of the light reflection, and the regu-

larity of the granulations distinguish the large unit from its neighbor at one side. A clearer view of the granulations that control the direction and intensity of the light reflection is seen in Fig. 4 which is at 1200 diameters magnification. The laminations of this print are the "etch figures" sometimes repressed by metallographers; they are not as easily brought out as cell borders and are obliterated by a little repolishing. Ordinarily



FIG. 4.—ULTIMATE GRANULES OR LAMINATIONS IN CAST COPPER; ETCHED WITH AMMONIACAL PEROXIDE AND NITRIC ACID. REFLECTIONS FROM FACETS OF LAMINATIONS DEFINE THE COLOR OF A NUCLEUS CELL; AS REFLECTION VARIES FROM FULL TO ALMOST NIL, COLOR CHANGES FROM WHITE TO BLACK. $\times 1200$.

their appearance is not desired because they subordinate the prominence of grain borders and inclusions.

Another print to demonstrate the difference between sutures and dendrite borders is Fig. 5, at 1500 diameters, where a suture line, somewhat resembling a twinning division, crosses at one side of the print and a quite different and well-filled crystal border separates a dark dendrite from its light-colored neighbor.

Nucleus Cells

The grains or, as the author prefers to call them, "nucleus cells" of recrystallized metal will be seen in many of the later prints. They have an important effect on the hardness and workability of the metal,



FIG. 5.—TYPICAL SUTURE LINE AND TYPICAL CELL BOUNDARY; ETCHED WITH AMMONIACAL PEROXIDE AND NITRIC ACID. DENDRITIC BORDERS MARK ABRUPT DISCONTINUITES BETWEEN DIFFERENTLY COLORED CRYSTALS; SUTURE LINES RESEMBLE TWINNING LINES. $\times 1500$.

but no studies on their origin or growth can be included at this time. One of the important structural observations that is inevitably made is

that the boundaries between nucleus cells are extraordinarily fine and give a much better contact between adjacent units than do even suture lines. Impurities crystallize along suture lines and frequently greatly intensify their demarkation; recrystallized metal is not divided with reference to previous units, so that bunches or rows of impurities may appear at any place within a nucleus cell. Single-crystal stock is not any purer than the metal in which the huge nucleus cell grew; the ultimate granulations of single crystals are interrupted by nodules of oxide, slag, sulfides, or whatever impurities were present in its multi-cell stage or were entangled when the metal crystallized from the melt.

When recrystallized, or nucleus cell, stock is cold worked or slipped, each shear plane marks a displacement somewhat similar to the border between neighboring nucleus cells. For this reason, cold-worked stock is difficult to etch for a strong delineation of grain borders; in the case of heavily deformed metal, it may be quite impossible to differentiate borders from slip markings. It is naturally more difficult to get good prints of heavily cold-worked stock than moderately worked stock, prints of which are shown.

Granules

The etch figures, or ultimate granules, of copper show with startling clearness when a chemically smoothed surface is etched with concentrated nitric acid. Fig. 4 was produced by merely dipping a suitable surface in concentrated nitric acid and rinsing as quickly as possible.

Little attention appears to have been given these granulations in copper or in other metals. While always conforming to the crystallographic habitat of the metal, the granules may have shapes dependent on the etching medium used. Rinne,¹ having studied the solution of salt crystals in different media and having found different forms for different solvents, says: "The particular form of a crystal constitutes a morphological symbol of the equilibrium of the balanced force fields that arise between its own substance and the materials around." The markings on copper conform to the isometric system. The constants determining the size of the laminations, or the distance between strata, or the sizes of cubic figures are at present unknown. The author has held that the granules are determined by some physical constant and have more significance than merely the progressive outline of the solution face.

Some support for the conception that the ultimate granules are actual physical subdivisions comes from the observation that the offsets in worked or slipped stock are of the same order of magnitude as the granules; this topic offers a promising field for further investigation. From all the prints of etched metals that the author has seen, and especially

¹ Frederick Rinne: "Crystals and the Fine Structure of Matter." E. P. Dutton & Co., New York, N. Y., 1924

from those at from 1200 to 9000 diameters magnification, there is no hint of any more minute texture or smaller order of crystalline units. This, of course, means that the chemicals used for etching have too gross



FIG. 6.—SET SURFACE OF A COPPER WIRE BAR; ETCHED WITH AMMONIACAL PEROXIDE. EDGE (BLACK) OF PRINT IS AT SURFACE OF BAR. $\times 50$.

an effect to disclose any demarkation even if it should exist. The subject of the effect of etching reagents is very fascinating.

TEXTURE OF CAST, WORKED, AND ANNEALED COPPER

Cast Copper

In continuing the study of copper further than to become acquainted with the three basic structural units—dendrites, cells, and granules—one promptly finds other important features. The oxygen eutectic is

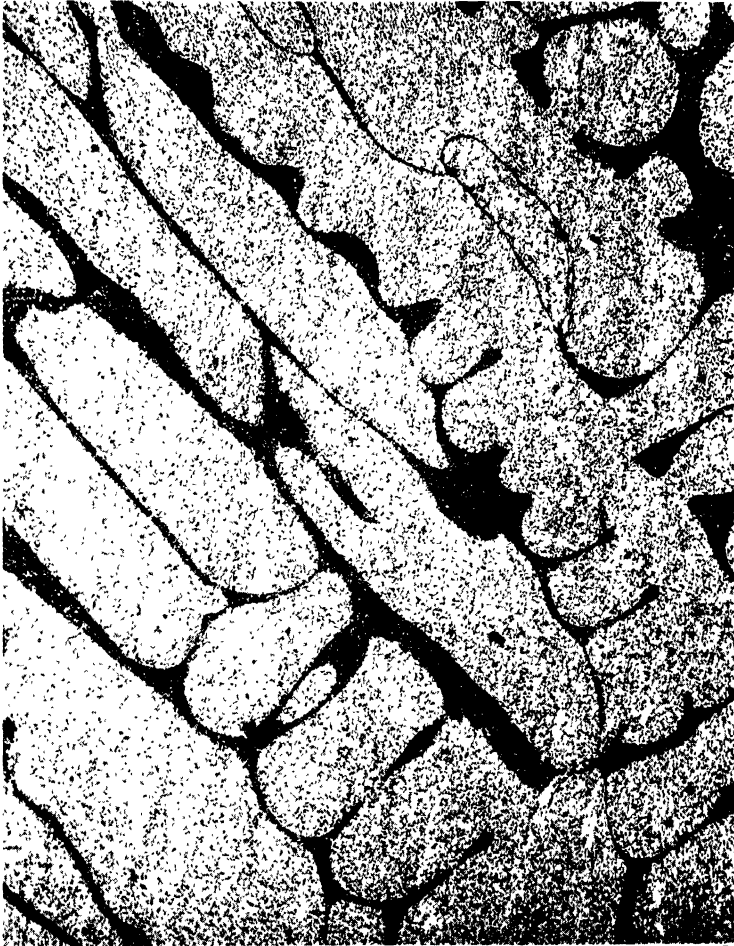


FIG. 7.—OXYGEN EUTECTIC DARK IN LOWER PORTION OF WIRE BAR; ETCHED WITH AMMONIACAL PEROXIDE. BAR HAS AN UNUSUALLY HIGH OXYGEN CONTENT. $\times 100$.

usually prominent in cast metal and its alteration product—oxide granules—can be found in practically all worked metal.

Cast copper commonly contains an amount of oxygen sufficient to make the cuprous oxide-copper eutectic noticeable as a structural component. It will be recalled that the eutectic is generally assumed as

consisting of 96.5 per cent. copper and 3.5 per cent. cuprous oxide, and that it freezes at 1063° , which is 20° below the freezing point of pure copper. If the eutectic is present in considerable amounts,



FIG. 8.—LONGITUDINAL SECTION THROUGH SMALL INGOT AFTER COLD-ROLLING; ETCHED WITH AMMONIACAL PEROXIDE. PRINT SHOWS ELONGATED DENDRITES AND TRANSVERSE BANDINGS (DARK). SEE NEXT FIGURE FOR DETAIL IN THE BANDINGS. $\times 100$.

it may be visible to the naked eye in polished sections. The eutectic frequently covers the surface of ingots to a varying depth, not

infrequently extending down $\frac{1}{8}$ in. Fig. 6, which is at 50 diameters magnification, shows a characteristic section through a thick layer of eutectic on the set surface of a wire bar. The entire surface consists of eutectic, which is gradually replaced by dendrites of massive copper until, at a depth of about $\frac{1}{5}$ in., a uniform admixture of eutectic and copper is found, which may persist throughout the bar. Fig. 7, at 100



FIG. 9.—NEW EQUI-AXED CRYSTALS IN BANDINGS OF FIG. 8; ETCHED WITH AMMONIACAL PEROXIDE. THIS GROWTH OF NEW CRYSTALS IS ONE CAUSE FOR SOFTENING OF OVERWORKED METAL. $\times 1500$.

diameters, was taken from deep in the corner of a wire bar and shows the texture of a rather high-oxygen metal.

Although cuprous oxide is a brittle mineral, it does not follow that copper is necessarily ruined by the presence of a considerable amount of eutectic. Surely cuprous oxide cannot improve the plasticity of copper, but that it is ruinous is not substantiated by the practical work in the drawing mills and by the fact that abundance of oxide may be found in

fine wires that have drawn satisfactorily. Many ferrous materials containing several per cent. of the extremely brittle carbide of iron are



FIG. 10.—HOT-ROLLED COPPER ROD; ETCHED WITH AMMONIACAL PEROXIDE. ETCHED FOR STRONG DELINEATION OF CELL BORDERS, REPOLISHED TO AVOID COLORING. ROWS OF IMPURITIES CROSS CELLS. SURFACE SHOULD HAVE BEEN ETCHED AND REPOLISHED AGAIN FOR COMPLETE ELIMINATION OF SCRATCHES. $\times 100$.

satisfactorily worked at temperatures when they are relatively less plastic than cold copper.

Cast Copper, Worked

Cast copper that has been cold worked has its dendrites elongated and its ultimate particles slipped to correspond to the change in shape of the specimen. Fig. 8 indicates the elongation of dendrites in a small specimen after cold rolling. This specimen probably had about 75 per cent. reduction and, besides the elongation of the dendrites, shows transverse bands that etched more deeply than the major part of the metal. With higher magnification the nature of the transverse zones



FIG. 11.—HOT-ROLLED COPPER ROD; ETCHED WITH AMMONIACAL PEROXIDE AND NITRIC ACID. SURFACE WAS FIRST ETCHED FOR CELL DEMARKATION, THEN LUSTER-ETCHED TO GIVE CELL CONTRAST. $\times 500$.

becomes clear; the bandings are spotted with nests of new and minute cells of recrystallized metal. These are the new equi-axed grains in haphazard orientation; Fig. 9 shows some of them at 1500 diameters magnification. The laminations of the new and well-defined units have no relation to the uniform slopes of the granules of the elongated dendrites.

This demonstration of the new units in cold-worked copper that has not been reheated probably explains the softening of the metal by too drastic cold working. The weakening and loss of cohesion by cold working may be complicated by another occurrence which, it is believed, can



FIG. 12.—COLD-DRAWN COPPER TROLLEY WIRE; ETCHED WITH AMMONIACAL PEROXIDE AND NITRIC ACID. CURVED CELL BORDERS AND NUMEROUS GRANULE OFFSETS AS WELL AS ELONGATION OF UNITS ARE EVIDENCE OF COLD-WORKING. ALL MATERIAL IS CRYSTALLINE. $\times 1500$.

be seen but which cannot be substantiated with prints—that is, a transverse fissuring of the heavily slipped grains.

Recrystallized Copper

Copper that has been hot rolled or cold worked and reheated shows a complete transformation with full development of equi-axed nucleus

cells. It is not difficult to so work and partly anneal copper that both the previous dendrites and the new units may be in about equal evidence; material of that sort, however, is not commonly produced. In worked and recrystallized stock, the impurities previously existing at suture lines of the borders of dendrites may appear in lines without reference to the new grains. In Fig. 10, which is at 100 diameters, can be seen several rows of imperfections that have no obvious relation to the new grains.



FIG. 13.—COLD-DRAWN COPPER WIRE, 0.184-IN. DIAMETER; ETCHED WITH AMMONIACAL PEROXIDE AND NITRIC ACID. LONGITUDINAL SECTION SHOWING SLIPPED AND ELONGATED CELLS. $\times 1500$.

The surface of this section was repolished nearly smooth, leaving the cell boundaries clear and showing but slight differentiation in the luster of the grains.

Fig. 11, at 500 diameters magnification, shows a surface of recrystallized copper etched for full luster effect. The cell borders are sharp

and straight and a full development of the cell granules gives a strong contrast from unit to unit.

Recrystallized and Worked Metal

The development of a suitable surfacing and etching technique has made possible the taking of pictures at about 1500 diameters magnification that show in considerable detail the slip structure of cold-worked copper. Longitudinal sections through worked metal indicate that the jagged offsets which result from slip are of the same order of magnitude



FIG. 14.—COLD-DRAWN COPPER WIRE, 0.051-IN. DIAMETER; ETCHED WITH AMMONIACAL PEROXIDE. LONGITUDINAL SECTION SHOWING SLIPPED AND ELONGATED CELLS. $\times 1500$.

as the ultimate granules of annealed stock. One is led to the inference that the ultimate granules are a structural reality and not the etch figures of a continuous but diminishing crystal.

A longitudinal section of a heavy cold-drawn wire, at 1500 diameters magnification, is shown in Fig. 12. The curved and serrated cell borders and the occasional transverse offsets instantly distinguish the worked

from the annealed stock. A comparison of the slip blocks of this $\frac{1}{2}$ -in. wire with those of wires 0.184 in. and 0.051 in. in diameter can be made by inspecting Figs. 13 and 14. The average cell size diminishes greatly with the decrease in wire diameter, but in each instance the slip blocks are



FIG. 15.—COLD-DRAWN COPPER WIRE, 0.184-IN. DIAMETER; ETCHED WITH AMMONIACAL PEROXIDE AND NITRIC ACID. END VIEW OF UNITS SHOWN IN FIG. 13. $\times 1500$.

apparently close to $\frac{1}{70,000}$ in. thick, when measured normal to the bedding plane.

Transverse sections through the 0.184-in. and 0.051-in. wires, respectively, are seen in Figs. 15 and 16. These prints are also at 1500 diameters magnification and plainly disclose the smaller cell units in

the smaller wire. In these transverse sections, the units with laminations at a slight angle with the plane of the section have etched out white.

None of the prints show wire or sheet that has received anywhere near the extreme amount of cold working. However, the prints do show that at this degree of working the metal is practically all crystalline and does not appear to contain appreciably more disorganized material than annealed stock. However hazy and indistinct the units may appear under the lower powers of the microscope or when the cell surfaces are not



FIG. 16.—COLD-DRAWN COPPER WIRE, 0.051-IN. DIAMETER; ETCHED WITH AMMONIACAL PEROXIDE AND NITRIC ACID. END VIEW OF UNITS SHOWN IN FIG. 14. $\times 1500$.

all in the same optical plane, there is no question about the sharpness and regularity of the crystal parts.

OXYGEN IN COPPER

The oxygen eutectic so commonly present in copper has a beautifully reticulated texture under the higher powers of the microscope. Fig. 17, which is at 1000 diameters magnification, indicates the striated and honey-comb varieties that evidently depend on the rods of oxide being normal

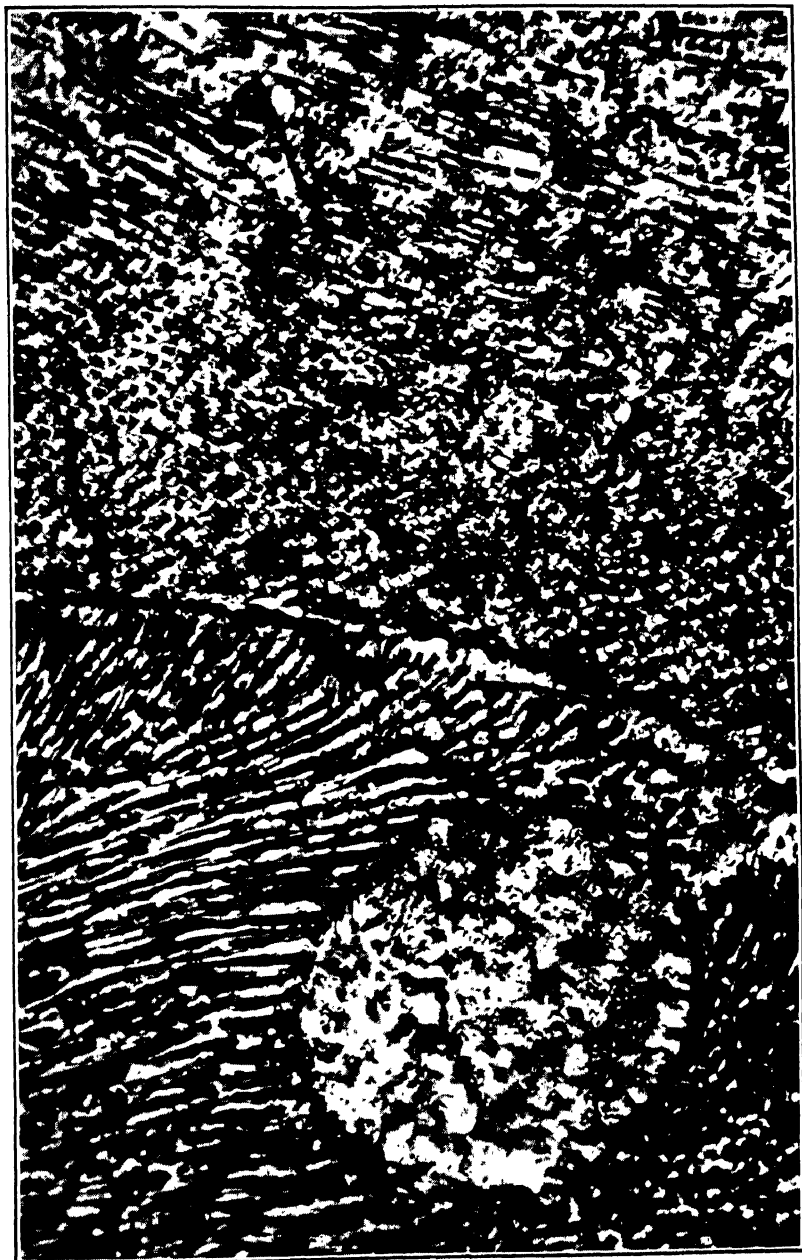


FIG. 17.—COPPER-CUPROUS OXIDE EUTECTIC WITH ONE SPOT OF MASSIVE COPPER; ETCHED WITH AMMONIACAL PEROXIDE. FROM SET SURFACE OF A SMALL UNTREATED INGOT. $\times 1000$.



FIG. 18.—COPPER-CUPROUS OXIDE EUTECTIC WITH SPOTS OF MASSIVE COPPER; ETCHED WITH AMMONIACAL PEROXIDE. SPECIMEN WAS REHEATED TO 800° C. FOR 30 MIN. $\times 1000$.

or parallel to the surface for each respective outline. Unit boundaries and spines of massive copper frequently interrupt the continuity of otherwise massive eutectic.



FIG. 19.—COPPER-CUPROUS OXIDE EUTECTIC AFTER HOT-WORKING; ETCHED WITH AMMONIACAL PEROXIDE. $\times 1000$.

There is no evidence at hand to demonstrate conclusively the coalescence of either oxide or copper component on a simple reheating of eutectiferous metal. Fig. 18 is of reheated stock and at 1000 diameters

magnification but offers little support for an opinion that reheating causes coalescence. The texture of the eutectic may be much coarser than in these prints, and with a coarse-grained eutectic it is perfectly plain that

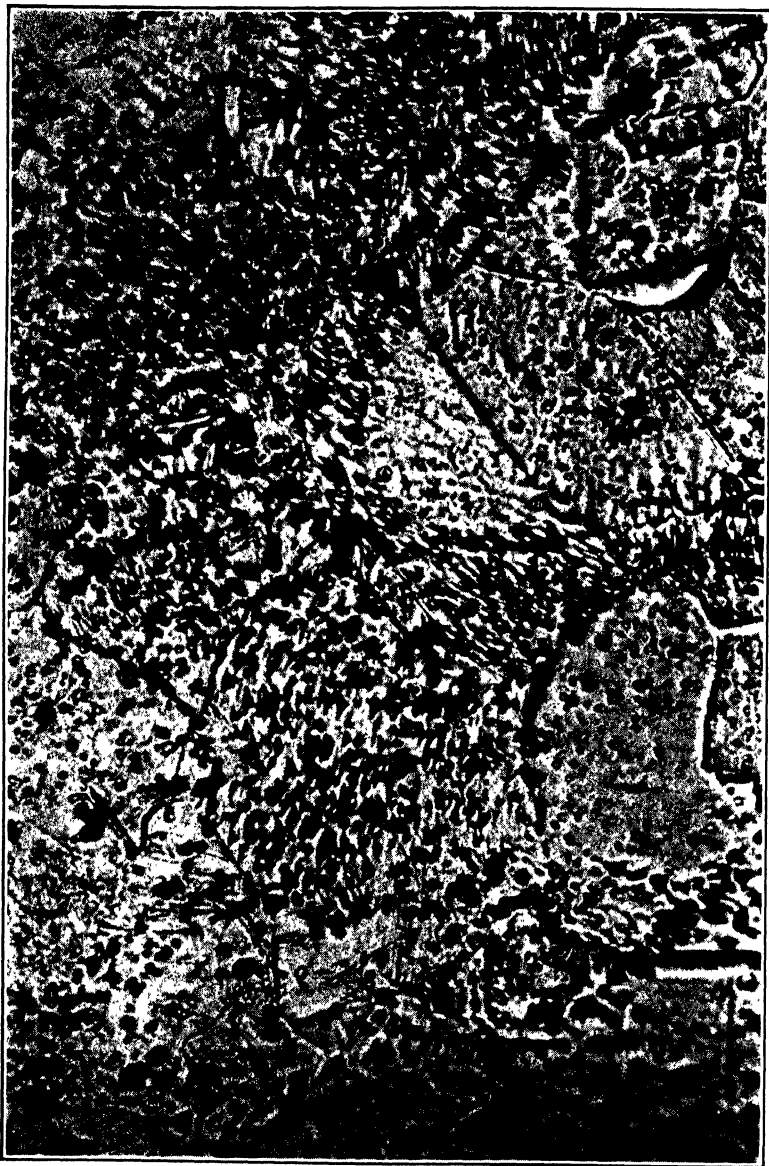


FIG. 20.—COPPER-CUPROUS OXIDE EUTECTIC, COLD-WORKED AND REHEATED; ETCHED WITH AMMONIACAL PEROXIDE. $\times 1000$.

the metal of the massive spines is continuous into the network of the eutectic copper.

Eutectiferous metal that has been hot-worked has new nucleus cells formed that crystallize without particular reference to the former eutectic masses. Fig. 19 demonstrates the latter point. This print, at 1000 diameters magnification, shows clearly the borders of previous eutectic masses and also shows how the new units include massive and eutectic copper promiscuously.

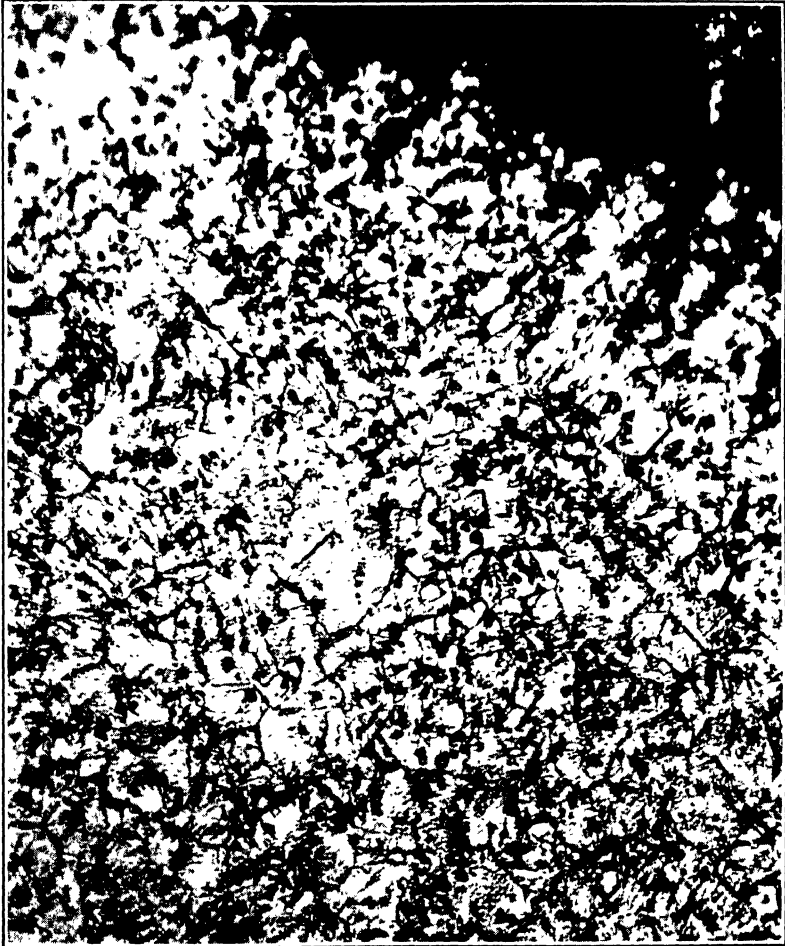


FIG. 21.—EDGE OF AN ANNEALED COPPER WIRE, 0.048-IN. DIAMETER, SHOWING OXIDE GRANULES FROM SET SURFACE OF WIRE BAR; ETCHED WITH AMMONIACAL PEROXIDE. OXIDE DROPLETS OCCUR SPARINGLY IN MOST OTHER SECTIONS OF WIRE. $\times 700$.

Metal that has been cold-worked and then reheated recrystallizes the same as hot-worked metal. Fig. 20 is from eutectiferous stock treated in the latter manner; again the previous eutectic borders are plain and the new cell boundaries cut through the eutectic fringes haphazardly.

The persistence of the eutectic, or set, surface of a wire bar through all the steps of hot rolling and cold drawing when metal is made into fine wires is one of the remarkable facts that only the microscope can detect. It has not been possible to study thoroughly the behavior of the set surface during wire-drawing operations, although it has been observed that the set section of the wire is frequently roughened and might be expected to be harder and flake more than other sides of the reduced wire-bar surface. Fig. 21, at 700 diameters magnification, shows the set edge of a



FIG. 22.—COLD-DRAWN COPPER WIRE, 0.124-IN. DIAMETER, ETCHED WITH 50-50 NITRIC ACID; LONGITUDINAL SECTION. $\times 500$.

wire 0.048 in. in diameter; the edge of the wire is roughened and this entire area is peppered with droplets of oxide from the original set surface of the wire bar. In a wire of this size, one or more sectors will contain oxide from the set surface of the wire bar, while most of the remainder of the periphery of the wire will be smooth and with few oxide spots. Under 1000 diameters and greater magnifications, the crystallites of cuprous oxide in wire appear like brilliant rubies set in a copper matrix.

ETCHING REAGENTS FOR COPPER

Ferric Chloride

Ferric chloride solution acidified with hydrochloric acid attacks copper slowly and reveals the large dendritic units in a satisfactory way.



FIG. 23.—HOT-ROLLED COPPER BAR; ETCHED WITH AMMONIACAL PEROXIDE. SLIGHTLY REPOLISHED TO GIVE SMOOTH CELL SURFACES. $\times 500$.

Fig. 1 was etched with ferric chloride and demonstrates how useful the reagent can be. For the finer structures, however, it is preferable to use some other reagent than ferric chloride because of its promiscuous attack and lack of selective erosion of the fine-structure.

Nitric Acid

Nitric acid in 50 per cent. solution does not dissolve copper so rapidly but that a good deal of texture can be revealed by its judicious use. Fig. 22, at 500 diameters magnification, is a longitudinal section through a cold-drawn wire; the texture of the metal comes out in passable form but the surface is marred by etch pits. The excessive solution of some



FIG. 24.—HOT-ROLLED COPPER ROD; ETCHED WITH AMMONIACAL PEROXIDE AND NITRIC ACID. CELLS ARE HIGHLY COLORED BY ATTACK ON ULTIMATE LAMINATIONS OF CELLS. $\times 1200$.

parts of the structure, giving large cavities, is the greatest defect of the nitric acid. It is on this account that nitric acid is not an acceptable reagent. There is a great difference in the effect of used and fresh solution. Fresh nitric acid reveals cell borders and granules sharply; used or partly saturated acid brings out the cell edges but rounds over the body of the cell without showing its fine laminations.

Ammoniacal Peroxide

If a little concentrated (at least 3 per cent.) hydrogen peroxide is poured into a small beaker of concentrated ammonia solution, there is produced a reagent that etches copper in a truly remarkable way—the surface is dissolved fairly uniformly and regularly, cell boundaries come



FIG. 25.—HOT-ROLLED COPPER BAR; ETCHED WITH AMMONIACAL PEROXIDE AND NITRIC ACID. $\times 1500$.

out strongly and pitting is largely eliminated. The best results do not come with a timid use of the reagent but by rapidly agitating the specimen, held with tongs, in the ammonia while peroxide is added at intervals

or let dribble to effervesce vigorously. The outer layers of flowed metal should be entirely dissolved away; a little rubbing on heaped tripoli on chamois by hand will help in giving relief to the cells and not make scratches that cannot be wholly eliminated by a final etching. Fig. 23, at 500 diameters, shows the effect of the peroxide etch and repolish on hot-rolled copper rod. Cell boundaries and twinings are boldly etched and the surfaces of the cells are sufficiently colored and in relief without



FIG. 26.—COLD-DRAWN COPPER WIRE, 0.074-IN. DIAMETER; ETCHED WITH AMMONIACAL PEROXIDE AND NITRIC ACID; LONGITUDINAL SECTION. $\times 1500$.

prominent attack on the ultimate granules or throwing any parts out of focus. It will be noticed that pitting is very moderate.

A considerable variety of effects can be produced by manipulation of the etching and repolishing. A longer attack with dilute solutions will luster etch, or color, the cells differentially according to the reflection from the granules. For the most contrasting coloring, the repolish should be minimized after the cells have been strongly delineated.

For uniform reflection from smoothed surfaces, the last treatment should be the repolish. Most of the structures represented in this paper were first outlined by the ammoniacal peroxide attack.



FIG. 27.—COLD-DRAWN COPPER WIRE, 0.074-IN. DIAMETER; ETCHED WITH AMMONIACAL PEROXIDE AND NITRIC ACID. TRANSVERSE SECTION AT COPPER ELECTROPLATED SURFACE OF WIRE; LARGER DIVISION OF PRINT IS WIRE SECTION. $\times 1500$.

Concentrated Nitric Acid

A section of copper smoothed and etched with ammoniacal peroxide to develop cell boundaries can be momentarily dipped in concentrated nitric acid and rinsed as quickly as possible, if it is desired to bring out the ultimate granules or laminations most prominently. The offsets of slip structure respond strikingly to this treatment. Fig. 24 is a section through hot-rolled copper rod at 1200 diameters magnification, as seen

after the double treatment. Deep-seated pitting results if an attempt is made to erode a surface chemically for cell boundaries with nitric acid instead of the ammoniacal peroxide, but a brief immersion in the concentrated acid discloses the fine structure. Figs. 4, 5, 11, 12, 13 to 16, and 25 to 27 show results obtained by the double treatment.

MECHANICS OF SURFACING COPPER

The prints shown have been photographed from surfaces prepared by a method that departs radically from the academic practice. The rapidly rotating disk covered with a yielding fabric and the use of a thin suspension of polishing medium have been dispensed with. The work can be done more quickly and easily, flatter surfaces can be obtained, and less metal is dragged to cover deep scratches if mechanical smoothing is subordinated to chemical attack. Large surfaces unquestionably require considerable time for cutting, filing, and smoothing, but those no larger than 1 in. square should be prepared ready for photographing in a few minutes. Small specimens, like wire sections, can be embedded in a fusible alloy, so that twenty or forty pieces can be prepared as one specimen and almost as quickly after the placket is cast.

Flat surfaces give superior optical results. A surface filed flat with a fine file can be perceptibly rounded by a few seconds contact with a fabric on a high-speed disk. Either the reflection of light or the contact with a steel rule quickly discloses a crowned surface. Files of varying coarseness are convenient for making flat surfaces, while with a metal as soft and yielding as copper it is well to finish with a broad fine file, over the wetted surface of which the specimen is carefully dragged in one direction only. A filed surface can quickly be made smooth enough for the first etching by a little rubbing on a well-used emery paper spread on plate glass.

The surface can also be smoothed by rubbing on the French emery papers Nos. 00, 000, or 0000 before the first etching or at any time subsequently. Wavy contours that result from the filing or too deep an etch are remedied by the use of the fine emery papers. The papers are only suitable for final stages of smoothing after they have had rough particles eliminated by use. The specimen is firmly held and pressed on the paper as it is rubbed to and fro; neither edge of the specimen should be given undue pressure so as to cause a rounding of the face.

The mechanical smoothing can be continued by rubbing on stiff tripoli heaped on a chamois skin stretched over a board impregnated with paraffin. Tripoli that has remained suspended for six 1-min. intervals in a 2-liter jar is settled in a wide-mouthed bottle, nearly all the supernatant clear water is poured off, and the stiff sediment is used on the wetted chamois. When rubbing on the heaped tripoli, a layer of abra-

sive is always maintained over the skin so as to avoid scratches. The tripoli treatment is especially efficacious for repolishing after etching.

To etch the mechanically smoothed surface, the specimen is held with the tongs just below the surface of some strong ammonia in a beaker and rapidly lowered and raised as the strongest peroxide is added in little dribbles or allowed to drop in continuously for about a minute. The chemical attack obviously takes place during the effervescence of the solution.

The repolishing of the etched specimen is done by grasping the piece firmly and rubbing to and fro on a pile of the tripoli, which gradually flattens out under the firm pressure that should be maintained. The tripoli becomes greatly blackened by the metal debris. A strong delineation of the structure requires that the etching and repolishing shall remove all of the mechanically flowed and smeared outer layers of the surface. This surface flowage was caused by the sawing and filing rather than by the rubbing on tripoli, for after the structure is well developed it is not damaged by the tripoli repolish so but that it reappears brightly after a little more etching. Depending on the work in hand, the specimen may be etched and repolished until the contours are pleasing or boundaries and granules are as striking as desired.

This general method of finishing specimens has been described and the results on several metals illustrated elsewhere.² In the case of copper, ammoniacal peroxide does the etching work to perfection, for it rapidly dissolves the scratched and flowed outer layers of metal to disclose boundaries, slip offsets and the homogeneity of the grains without making deep pits or ruining the optical plane of the surface. Proper repolishing will leave the nucleus cells plane and sharply outlined by grain borders, or a last dip in concentrated nitric acid will give each cell a chiseled surface by the development of the etch granules.

Fig. 25 was prepared according to the method just described. The effect of bringing out the granules in each nucleus cell is to give strong contrast from cell to cell. The field is fairly large and uniformly in focus for a print at 1500 diameters. This method of etching has been severely criticised by competent metallographers, who say that detail is impossible to obtain. That objection can be answered by counting some of the finer lines in one of the cells where the laminations are at a steep angle; in one unit nine lines are visible in $\frac{1}{4}$ in., a resolution of 54,000 lines to the inch. A print made at 2500 diameters gives no finer resolution and, because of the increased haziness of the lines and fewer cells, is less pleasing.

Fig. 26 is taken from a longitudinal section through a cold-drawn wire magnified to 1500 diameters; it is one of a series of thirty sections

² H. B. Pulsifer: "Structural Metallography." The Chemical Pub. Co., Easton, Pa. 1924.

embedded in fusible alloy, all being prepared at the same time. One of the slipped units shows six offsets in $\frac{1}{8}$ in.—a resolution of 72,000 lines to the inch. When a section of this sort of stock is etched in nitric acid, certain of the units are apparently entirely excavated to give great holes and disfigure the picture; the restrained but illuminating effect of the peroxide etch is very gratifying. Fig. 27 is a transverse section from one of a series of embedded wires. In order that the edges of the wires might be observed, the specimens were electroplated with copper before mounting. The electroplated edge is at the banded zone of the smaller section of the print, the two materials being separated by the black line caused by the etching. As the print is at 1500 diameters and granular metal is at the very edge of the black line, any vitreous metal on the surface of the wire is probably less than $\frac{1}{30,000}$ in. thick.

For mounting wire sections, it is convenient to place longitudinal and transverse pieces in fusible alloy and then file down the placket until all wires are well exposed. As fusible alloy containing 50 per cent. bismuth melts below the boiling point of water and will cool farther in a few seconds after pouring, there is no danger of annealing even the most cold-worked stock. It is convenient to bend a short section of wire sharply at right angles against a piece of soft wood with pliers and then file the outside of the unsqueezed leg to a flat longitudinal surface. The area near the bend is not used. Notches are filed in the squeezed end of the wire and similar notches in one end of straight sections about $\frac{1}{2}$ in. long. The notches are to prevent subsequent movement of the wire in the mount; they fill with the mounting alloy and hold the wires from twisting or pushing back when the placket is filed or rubbed. A row of flattened pieces is closely laid on a bit of cardboard and each piece held down firmly with a pin pushed through so that its head pinches down on the wire. Wires may be laid so closely that only the thickness of the pin separates them; slightly wider spacing is recommended so that the fusible metal can flow better about each wire. A hole is made at the end of each bent wire so that the straight section of the same size can be pushed through. The filed notches in the wires come about $\frac{1}{8}$ in. above the board. A length of flexible copper strip $\frac{1}{4}$ in. wide is bent about the group of wires, held down firmly with tongs, and fusible alloy poured to a depth of about $\frac{3}{16}$ in. The cardboard can be moistened and pulled away from the pins and straight wires; the pins and wires are then cut short against the placket and the whole mount prepared as one specimen. A placket of forty specimens can be finished ready for photographing in two hours, or less, without hurrying.

An etched copper surface tarnishes very rapidly. An etched surface can be dried by pressing the rinsed face against a compress of clean but long-used cotton or linen. Blowing the surface, or holding in front of a

small fan, dispel the last film of moisture quickly. Mounted specimens are more inconvenient than single massive ones, because a film of solution gets in the crevices and gradually flows out and discolors the sections. Immersing in a mixture of equal parts of absolute alcohol and ether, before the pressing, will help considerably. If the oil-immersion objective is to be used, the cedar oil should be spread over the surface the moment the placket is taken away from the current of drying air.

The photomicrographs shown here were made with a Bausch & Lomb metallograph. The 2-mm. objective with oil immersion served for the higher powers. A Wratten filter, B-58, was used in front of the arc and commercial-ortho films recorded the image. Magnifications were determined with a micrometer scale, the graduations of which were measured on the ground glass of the camera. The prints were made on the several grades of Nova-Gas photographic paper supplied by Gaevent & Co. of New York.

DISCUSSION

J. S. VANICK, Bayonne, N. J. (written discussion).—Some 4 or 5 years ago, I was engaged in an attempt to resolve the inner structure or internal organization of the metallic grain and found the structural condition which Mr. Pulsifer describes here for Cu in iron, copper, brass, lead and possibly aluminum. The whole subject might be dismissed by calling the structures "etch figures" and letting it lay there, but one is struck with the amazing uniformity and symmetry with which a single grain may be resolved into smaller symmetrical units which show what I had called a block-plane assembly. This block-plane assembly may again be resolved into unit blocks which I called crystal elements and element planes. Fig. 24 of Mr. Pulsifer's paper illustrates some of these patterns; the first in the strikingly uniform frequency of the plane out-crops along the edges of the figure and the second in the regular periodicity of the smaller blocks into which the surface of such a plane seems to be divisible as is shown in the center of Fig. 24. The microscopic subdivision does not end there in all cases, but frequently will perform a further resolution of one of these blocks again into a finer set of bedding planes and a sequence of smaller notches. This usually brings us to the end of the resolving power of the microscope and we have gone to less than half of the resolving power of the X-ray and made two resolutions. In a hypothetical layout of the organization of a grain, I had carried the subdivision four stages further which ended the partitioning at the atom and provided for: the atomic unit or lattice constant for metals on a single simple lattice; combinations of two or more atomic units assembled on a compound lattice, and conversion of the latter into a symmetrical crystal form. It did not subdivide the atom, which, as Dr. Foote showed in his lectures, is capable of division into three or four additional energy levels.

As I said before, the entire subject may be dismissed as "etch figure" phenomena and it may be admitted that the polyhedral grain which the low powers of the microscope reveal, is composed of the planes of atoms which the X-ray develops; but the etch-figure study leaves you conscious of the existence of these block planes and blocks and finer planes with their notches all exhibiting a successively finer subdivision, each subdivision possessing an individual periodicity which suggests successive stages in the development of that grain. Stead in 1898 revealed the block-assembly in silico-ferrite grains in a macroscopic degree, and finer subdivisions of such blocks may be resolved into their bedding planes by microscopic methods. The striking periodicity of the planes and blocks in the etch-figure patterns seems to require the grain-organization explanation which Mr. Pulsifer mentions, and which I have elaborated. The X-ray picture of a grain places the atoms in planes, in an ideal spacing too fine to resolve microscopically, but in supporting this grain partitioning I feel consoled to think that the extremely high resolving power of the X-ray was too fine to register these coarser-dimensioned features.

A patient study of the periodicity of planes and blocks in etching figures would doubtless throw more light on stress-flow and stress-distribution in grains of worked metals, upon solidification phenomena in cast metals and upon cleavage, slip, etc., in grains.

H. B. PULSIFER (written reply to discussion).—As Mr. Vanick intimates, all metals probably have the fine, block-crystal structure which I call the granules. In my test, mentioned in the paper, there are prints that indicate the granules of copper, iron, aluminum, tin, lead, bismuth and germanium. These units appear to be the finest visible structural elements in metals, not because of the lack of resolving power in current metallurgical microscopes, but because the etching reagent has not differentiated finer divisions.

The dendritic boundaries of metals are the easiest structural divisions to outline because impurities are usually concentrated along them and because the granules of neighboring units are differently oriented. The nucleus-cell boundaries likewise disclose themselves readily because of the different orientations of the granules in each neighboring cell. The metal in the zone between two cells also dissolves preferentially before the main internal section is appreciably attacked. An etching reagent that will uniformly attack and disclose the ranks of the ultimate granules must have a selectiveness and delicacy exceeding that demanded of most commercial etching mediums. It is the fortunate combination of the two reagents that has made the delineation of the structure of copper so successful: the peroxide etch dissolves off the outer layers of poorly crystallized metal and leaves the surfaces of the cells fairly smooth; the nitric acid then attacks the surfaces just enough to bring into relief the ranks of granules. Nitric acid is a poor reagent for dissolving off the scratched

and glassy surfaces of the cells and the perioxide is very poorly selective for revealing the ranks of granules. To disclose another and a finer order of units in the granules of copper it would appear plausible that some other and more delicate reagent would be necessary. Mr. Vanick does not state what reagents he uses to reveal the sub-granules.

Now that we have a slip-interference theory to account for some of the elements of hardness, strength and plasticity in metals previous speculations become strikingly inadequate and vacuous. There is yet very much to be cleared up in regard to the properties of metals. If microscopical units of different orders of magnitude exist in the nucleus-cells, as Mr. Vanick and I are in accord upon, then whatever can be learned about the smaller units will have bearing on the mass properties of metals. Surprisingly good work is being done with magnifications up to 9000 diameters and if the technique of surfacing and developing structure can be made to keep pace there is a wealth of knowledge to reward the skillful and patient metallographer.

F. W. HARRIS, Baltimore, Md.—The use of strong etchants in preparing copper for the microscope is valuable in some ways and not in others. Its chief value is in developing macrostructures and in developing structures of extremely cold-worked metal, but for viewing the more delicate tracerics of fine eutectics and impurities in grain borders, I think a lighter and more easily controlled form of etching is advisable.

The etching which we have developed at Baltimore and which has given very good results indeed is a 50-50 mixture of $2\frac{1}{2}$ per cent. ammonium persulfate solution and 50 per cent. ammonium hydroxide solution, used as a polish-attack by rubbing the specimen on a white felt cloth or leather chamois with finely levigated cream of alumina and applying the etching as solution as the specimen is rubbed.

Mr. Pulsifer states in his paper "there is no evidence at hand to demonstrate conclusively the coalescence of either oxide or copper component on a simple reheating of eutectiferous metal," and he shows Fig. 18 to be of reheated stock of 1000 diameters magnification, which offers little support for an opinion that reheating causes coalescence. Our experience has been to the contrary. We have very good evidence that heating copper at 900° C. will produce coalescence very rapidly.

H. B. PULSIFER (written discussion).—Inspection of a good many reheated wire bars, hot-rolled rods and wires drawn from heated and annealed copper shows cuprous oxide in units about the size of the particles originally present in the eutectic of the ingots. This checks with the results of the experiments given in the paper. Of course, this does not preclude the possibility of the oxide coalescing under other conditions. It will be well worth while, both scientifically and industrially, to know just what the conditions are under which the oxide coalesces rapidly.

Symposium on Gas in Copper

[A session of the Institute of Metals held during the February, 1926, meeting of the Institute, was devoted to a symposium on "gas" in copper. S. Skowronski, Perth Amboy, N. J., was chairman. On the program were papers by T. S. Fuller; W. H. Bassett and J. C. Bradley; Susan B. Leiter, and W. H. Bassett and H. A. Bedworth. These papers follow the chairman's introductory discussion.]

S. SKOWRONSKI, Perth Amboy, N. J.—There are today two groups of metallurgists, one group who believe in oxygen-free copper and another group who believe that oxygen is absolutely essential in copper; not that the two groups disagree, but that a certain grade of work calls for oxygen-free copper, while another grade of work does not.

I can sum up the problem by reading the abstract of an article by Frederick Johnson of Great Britain in *The Metal Industry* of Sept. 4, 1925.

Few, who have watched the trend of things during the last two decades, can have failed to notice the steady growth of opposition to the prevalent use of copper in the "tough-pitch" condition, which for many ages enjoyed an unchallenged supremacy. Broadly speaking, there are two schools of thought in the metallurgical world, one holding the view that copper containing a small proportion of oxygen is an eminently suitable material for users, the other expressing its preference, in no hesitating or uncertain manner, for copper from which oxygen has been removed by means of a deoxidizer.

In the old days, before the advent of the converter and the electrolytic refining process, the copper of commerce was so impure that the presence of oxygen was imperative in order to neutralize the influence of impurities which militated against the hot-working properties of the metal. For electrical purposes, oxygen must be present, because sound bars and billets cannot be produced without it, except at the expense of electrical conductivity. For most engineering purposes, however, electro-deposited copper may be used either by itself or with the addition of alloying elements, *e. g.*, arsenic and nickel, which experience has proved to be beneficial, such copper being freed from oxygen by the aid of a deoxidizer, *e. g.*, phosphorus.

Such material has positive advantages over "tough-pitch" copper as at present produced from refinery furnaces. It has greater toughness and malleability, and is immune from the action of reducing gases at high temperatures, the destructive action of which, in the case of "tough-pitch" copper, is well known.

The reasons why there has been no wholesale replacement of "tough-pitch" copper by deoxidized copper are commercial in nature; copper can be more economically melted in large-capacity furnaces which lend themselves to the poling process and are not so suitable for control of uniformity of action of deoxidizers as the smaller electric or crucible furnaces, whilst they are also more convenient for the production of very large castings. Moreover, the equipment of most large copper manufacturing plants is designed for casting "tough-pitch" copper in open moulds, *e. g.*, wire bars and cakes, and these could not be used for deoxidized copper, which must be cast in vertical moulds as in brass-shop practice. Further, there are still certain impure brands and

classes of copper that can most economically be treated for the production of "tough-pitch" copper by the poling process. It is these reasons, all associated with economy of production, which justify the continuance of production of "tough-pitch" copper.

Relative to the amount of oxygen in copper, the article continues:

Too much insistence cannot be placed on the necessity for obtaining this minimum, which should be below 0.05 per cent. Double this amount is often found, and, in view of recent progress in the metallurgy of copper, this should be regarded not only as avoidable, but as intolerable, in high-grade metal.

Impurities such as lead, bismuth, antimony and sulphur necessitate the protective influence of oxygen, but such impurities should be in negligible amounts in high-grade copper.

Embrittlement of Copper by Hot Reducing Gases

T. S. FULLER, SCHENECTADY,* N. Y.

(New York Meeting, February, 1926)

VARIOUS phases of the embrittlement of solid copper containing oxygen by the action of reducing gases at high temperatures are familiar to readers of metallurgical literature through the work of many experimenters.

In 1900, Heyn¹ recorded observations of copper being heated in hydrogen with the development of fine cracks, the result of the formation of steam within the metal through the action of hydrogen on the copper oxide usually found in copper.

Archbutt,² in 1905, published the results of experiments, showing that all oxygen can be removed from copper by heating to redness, for several hours, in hydrogen. Inter-crystalline cracks and extreme brittleness developed. Archbutt attributed the brittleness to the reduction of oxides present in the copper.

Bengough and Hill,³ in 1910, encountered the now well-known embrittlement at the outset of their investigation and stated in their paper:

It soon became evident that the effect of any heat treatment depended largely on the presence or absence of reducing gases in the atmosphere of the furnace, as well as on its temperature. Hence it became necessary to adopt a somewhat elaborate scheme of heat treatment.

The authors found embrittlement in separate experiments due to both hydrogen and carbon monoxide and concluded that: "The gases ruin the alloys after being heated to about 650° C. in their presence."

Ruder,⁴ in 1916, reported the results of a series of experiments made by heating commercial and deoxidized copper in hydrogen, carbon monoxide, carbon dioxide, and steam. In agreement with other writers, he found that copper containing oxygen was made brittle by reducing gases, while the deoxidized metal remained unaffected. In the case of

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¹ E. Heyn: *Zeitschrift des Vereins deutscher Ingenieure* (1900) **14**, 16.

² L. Archbutt: Estimation of Oxygen in Copper. *The Analyst* (1905) **30**, 385.

³ G. D. Bengough and B. P. Hill: The Properties and Constitution of Copper Arsenic Alloys. *Jnl. Inst. Met.* (1910) **3**, 34.

⁴ W. E. Ruder: The Brittleness of Annealed Copper. *Trans. Am. Electrochem. Soc.* (1916) **29**, 515.

dry hydrogen, no brittleness could be discovered after heating samples to 400° C. for 2 hr. After 31 hr. at this temperature, however, a decided weakening had occurred. At 500° C. a decided embrittlement had taken place after heating for 2 hr. In the case of wet hydrogen, embrittlement did not take place until the metal had been heated to 600° C. In the case of carbon monoxide, brittleness was not observed until a temperature of 850° C. had been reached.

Pilling,⁵ in 1918, in discussing the mechanism of the action during exposure to reducing gases, says:

If hydrogen is physically soluble in solid copper at high temperatures, this gas would penetrate the metal, attack and reduce the grains of Cu_2O , with the formation of steam. After this reduction, the volume of the copper is but 60 per cent. of the volume of the Cu_2O from which it was reduced, thus leaving voids marking the site of the original oxide granules and approximating 40 per cent. of the space formerly occupied by them.

If steam is physically less soluble in copper than hydrogen, it will accumulate in these pockets at a rate faster than it can dissolve in the copper and diffuse away, and the net result of the reaction would be the formation of a quantity of steam within the voids left by the Cu_2O and at considerable pressure. A rough calculation of the magnitude of the pressure possible at 800° C., assuming the steam to be completely insoluble in the copper, showed that 8000 to 9000 atmospheres would develop if there were no yielding in the copper.

The rate of diffusion of hydrogen, steam, carbon monoxide and carbon dioxide through copper at 700° C. was measured and found to be:

GAS	DIFFUSION RATE
Hydrogen.....	1000
Steam	65
Carbon monoxide	17
Carbon dioxide	0 6

It will be seen that hydrogen will diffuse into copper approximately 15 times as fast as water, formed by the reaction of hydrogen on Cu_2O , can diffuse out and, similarly, that carbon monoxide diffuses through copper about 25 times faster than the carbon dioxide formed when it reduces the cuprous oxide.

This result seems to confirm the above explanation, that the weakness experienced by copper containing disseminated oxide, after exposure to reducing gas at high temperatures, is due to the internal fractures produced by the expansive action of a gas which is formed by the reduction of each oxide granule at a rate much faster than that at which it can dissolve in the copper and diffuse away.

The work reported by Moore and Beckinsale⁶ agrees with that of other investigators and in addition points out that copper containing as little as 0.026 per cent. oxygen is seriously embrittled by the hot reducing gases. "The lower the oxygen content, the higher is the temperature required to cause similar injury."

⁵ The Action of Reducing Gases on Hot Solid Copper. *Jnl. Franklin Inst.* (1918) **186**, 373.

⁶ H. Moore and S. Beckinsale: The Action of Reducing Gases on Heated Copper. *Jnl. Inst. Met.* (1921) **25**, 219.

The author,⁷ in 1922, called attention to the extreme sensitiveness of the action of reducing atmospheres on heated copper and concluded as follows:

The desirable mechanical properties of ordinary copper are completely destroyed on electrically heating to 800° C. in air for 1 hr. in an iron pipe filled with seas and—two substances which are not usually regarded as sources of reducing atmospheres.

The writer has regarded the small amounts of carbon in the steel and small amounts of organic matter present on the sea sand as sources of this reducing atmosphere.

The ductility of the metal is destroyed by intergranular cracks which probably result from the formation, accumulation, and subsequent pressure of a gas resulting from the reaction of the reducing gas upon the oxide present in the copper.

Oxygen-free copper is not affected by this treatment.

If finely divided Al_2O_3 be substituted for the sea sand, and a porcelain, electrolytic iron, or copper tube, for the iron pipe, the ordinary copper may be heated to 800° C., without damage.

Ordinary copper becomes brittle when heated in a steel pipe packed with Al_2O_3 ; or when heated in a porcelain tube packed with sea sand, unless the sand be first heated 4 hr. at 600° C., to remove organic matter.

The purpose of the present paper is to report several instances of copper embrittlement, caused by hot reducing gases, that have come under the observation of the author and which may be correctly termed "factory troubles."

MICROSTRUCTURE

The structure of fully annealed copper that has been heated under non-reducing conditions is shown in Fig. 1. The "tight," sharply defined, grain boundaries and square-corner grains of the cubic structure are characteristic of copper treated in this way. Fig. 2, on the other hand, is typical of copper heated to a high temperature under severely reducing conditions. The intergranular cracks and rounded grains are in direct contrast to the structure in Fig. 1. In the examples of brittle copper cited in this paper embrittlement had progressed to a marked degree. No samples showed the ductile structure of Fig. 1; on the other hand, none of the conditions described were as severe as those to which the sample having the structure shown in Fig. 2 was exposed, so that none of the examples showed as badly disintegrated structures.

RAIL BONDS AND SOLDERING IRONS

Among the first cases of copper containing oxide being made brittle by the action of reducing gases to come to the writer's attention were some rail bonds similar to the one shown in Fig. 3. In the process of manufacture, after preparing the cable section of the bond, the terminals

⁷ T. S. Fuller: The Extreme Sensitiveness of the Action of Reducing Atmospheres upon Heated Copper. *General Electric Review* (1922) **25**, 184.

were drop-forged on the ends at a red heat. Oil-fired furnaces of the muffle type were used for heating, and not infrequently the strands of the cable became extremely brittle. Observation showed that if the combustion of the furnace was so regulated that reducing conditions existed in the region occupied by the rail bonds, embrittlement occurred; but that

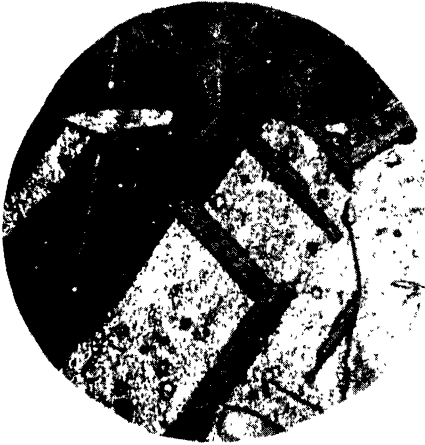


FIG. 1.—COMMERCIAL COPPER, ANNEALED. $\times 75$.

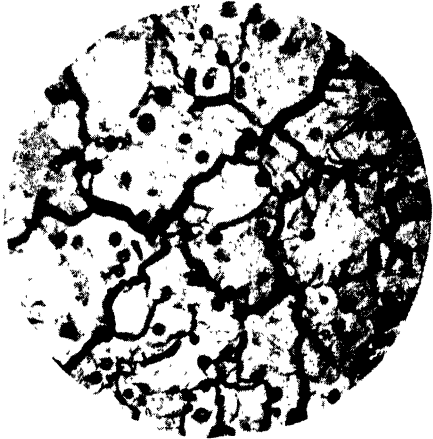


FIG. 2.—COMMERCIAL COPPER HEATED IN HYDROGEN 2 HR. AT 850°C . $\times 200$.

if oxidizing conditions predominated, no embrittlement took place. The remedy for this embrittlement was therefore obvious.

Another example is the calorized electric soldering copper, or soldering iron as it is commonly called, shown in Fig. 3. In the calorizing process, the copper is heated in powdered aluminum in a hydrogen atmosphere for 2 hr. at a temperature of 800°C .; this produces a diffusion of aluminum

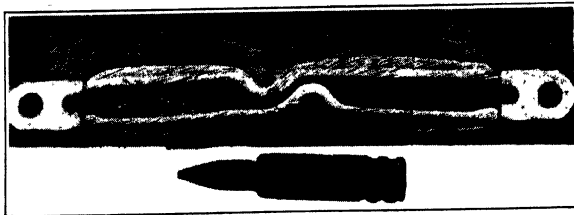


FIG. 3.—RAIL BOND AND CALORIZED SOLDERING COPPER.

into the surface of the copper, forming a coat of aluminum bronze that is highly resistant to oxidation at high temperature. The long heating at the high temperature in hydrogen produced blisters and cracks which were highly undesirable; on the surface of the soldering irons, the difficulty was overcome by using copper free from oxide.

WATER-COOLED X-RAY ANODE

Not all cases of copper embrittlement caused by reducing gases are as obvious as these just mentioned. The phenomenon was found to be the cause of very minute leaks in high-voltage, Coolidge *x*-ray tubes, the successful operation of which depends on maintaining a very high vacuum, which of course can be accomplished only by the use of absolutely non-porous materials in the construction of the tube. Among the parts to be suspected and considered as possible sources of leaks was the water-cooled anode, shown in Fig. 4. The anode is made by casting copper in vacua against one side of a tungsten disk, and subsequently recessing the copper to receive a flat spiral of $\frac{1}{8}$ -in. copper tubing *A*,

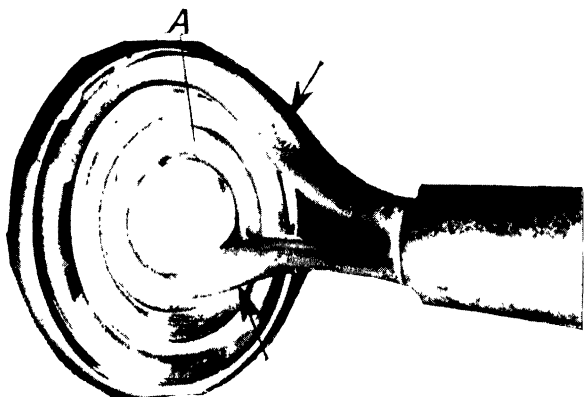


FIG. 4.—WATER-COOLED ANODE FOR HIGH-VOLTAGE COOLIDGE X-RAY TUBE.

through which water flows when the tube is in operation. The spiral is then silver-soldered in place by heating in vacua by means of a high-frequency current.

Microscopic examination of the copper tubing, at the points indicated by the arrows, showed the first stages of the characteristic intergranular embrittlement caused by reducing gases, resulting in a porosity sufficient to ruin the vacuum in the tube. The trouble was caused, during the soldering operation, by the reduction of the oxide in the copper by vapors from oil or other organic matter remaining on the anode parts after machining and was corrected by using tubing made from oxygen-free copper.

TWENTY-KILOWATT TRANSMITTING-TUBE LEADS

Brittle copper resulting from the action of hot reducing gases on metal containing oxide was found to be the cause of the difficulty that developed with the flexible leads used in the manufacture of pliotrons of 20-kw. capacity. Such a lead is made by silver-soldering a copper cable, made

of strands of wire 0.0045 in. in diameter, to a tungsten rod. Embrittlement occurred near the joint indicated by the arrow due to the reduction of oxide in the wire by the reducing gases of the flame which came in contact with the wire during the soldering operation. The trouble has been overcome by first annealing the copper cable, as described by Miss Leiter.⁸ Such an annealing serves to agglomerate the cuprous oxide present in such a way that the copper is not embrittled by hot reducing gases.

LEADS FOR 250-WATT TRANSMITTING TUBES

Trouble similar to that just described was found in the leads for U. V. 204 vacuum tubes. In the manufacture of these leads, one end of the composite copper-nickel-steel wire is electrically welded in an atmosphere of hydrogen to a tungsten wire, and the other end is welded to a copper cable. Embrittlement of the cable was noticed near the latter joint; it was caused during the welding operation by the reduction of cuprous oxide by hydrogen.

ENAMELED WIRE

Perhaps one of the most unexpected cases of embrittlement occurred in fine copper wire during an enameling process. Wire 0.003 in. in diameter is regularly passed through an enamel bath, at the rate of 125 ft. per min., and then into a 48-in. furnace held at a temperature of 430° C. The wire is ordinarily given five coats of enamel, being passed through the furnace after each coat. The reducing conditions, due to the vapor of the enamel solvent and the decomposition of the enamel base, that prevail in the furnace, produced a brittle wire. Under the microscope, a section showed clearly the condition resulting from reducing atmospheres at high temperatures. The embrittlement in this instance has been overcome by removing the reducing atmosphere surrounding the wire by drawing air through the furnace.

FLEXIBLE SHUNTS FOR CONTACTORS

An additional example involving embrittlement has been found in flexible shunts for contactors. The shunts are made of flat, braided cable, the individual strands of which consist of copper wires 0.004 in. in diameter. During the process of manufacture, the shunts often lie in the shop for some time, when they become tarnished by atmospheric corrosion. It was suggested that after being tarnished the shunts might be brightened quickly and efficiently by heating in a hydrogen atmos-

⁸ Susan B. Leiter: The Annealing of Commercial Copper to Prevent Embrittlement by Reducing Gases. Issued as Paper No. 1523E, with MINING AND METALLURGY, February, 1926.

phere. This was done at different temperatures and for different lengths of time, with very unsatisfactory results, because all sets of conditions that "cleaned up" the surface of the cable produced embrittlement, and all sets of conditions that left the wire mechanically strong and ductile failed to brighten the surface. An alkali method of cleaning was later found to give satisfactory results.

CONCLUSION

Realizing that the problems associated with copper embrittlement due to hot reducing gases are diverse and that the results cannot always be as easily explained as one might suppose, the author has endeavored to contribute helpful facts by describing examples of embrittlement that have occurred during the manufacture of a variety of devices. The subject of embrittlement due to reducing gases must be of interest alike to producers and fabricators and must be taken into account by every one who has occasion to apply heat to copper.

DISCUSSION

H. S. RAWDON, Washington, D. C. (written discussion).—A helpful way of looking at this problem, at least from the viewpoint of the structural change involved, is to consider it as a specific case of the more general problem of intercrystalline brittleness of metals. It is well established that the normal fracture of the common metals broken in tension at ordinary temperature is *transcrystalline* in character; at elevated temperatures, however, the fracture of the same metals broken in a similar manner tends to be *intercrystalline*. In other words, this characteristic behavior of metals indicates that the "bond" holding the grains together is, at elevated temperatures, weaker than the "bond" existing throughout any individual grain and holding it together. The temperature which must be employed to develop this structural feature varies, of course, with the metal tested.

It should not be surprising therefore, that, if the intercrystalline "bond" is still further weakened, the metal will show intercrystalline brittleness, and that this brittleness may persist in the metal after it has been cooled to room temperature depending upon the severity of the weakening of the bond. This weakening of the intercrystalline "bond" may be brought about in a variety of ways. In the case of the metal under discussion, copper, the pressure resulting from the formation of gas throughout the interior is an adequate and sufficient explanation of the change which results in the properties of the metal. Further, it would seem reasonable to expect, that, for a maximum embrittling effect, the chemical constituent (cuprous oxide) which by its reaction with the reducing atmosphere in the annealing furnace gives rise to the gases which

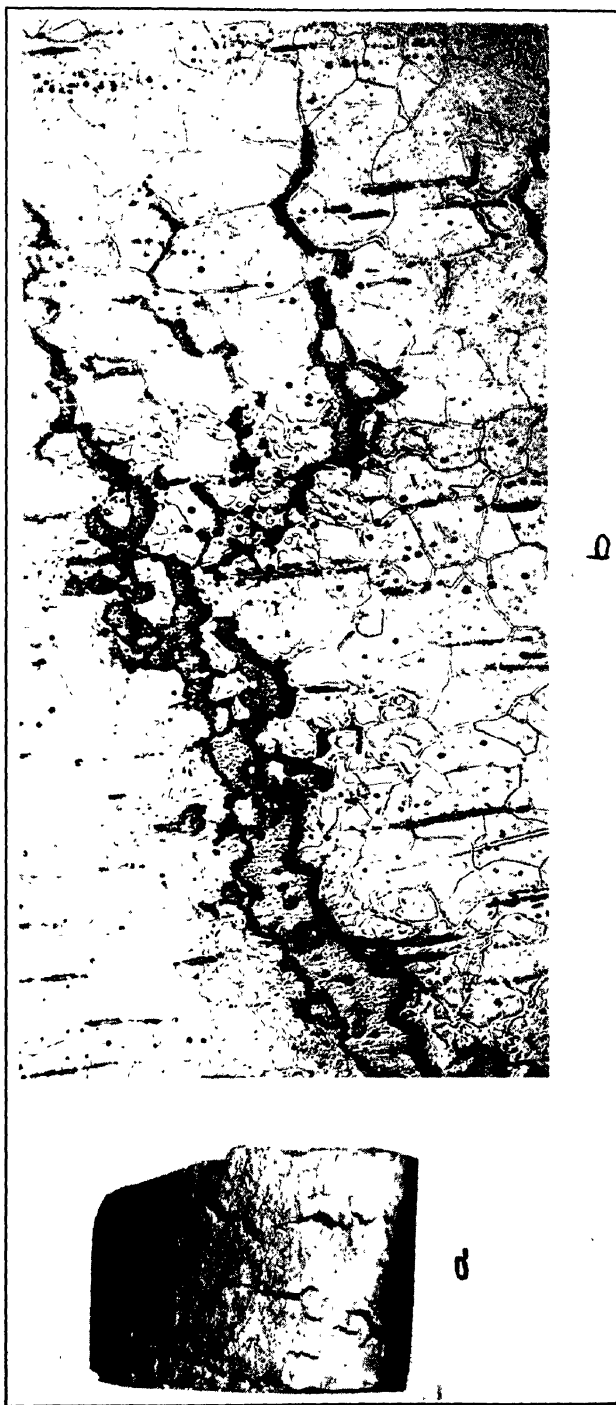


FIG. 5.—INTERCRYSTALLINE BRITTLENESS INDUCED IN WROUGHT IRON BY HEATING IT IN MOLTEN COPPER. THE IRON WAS STRESSED BY SLIGHT BENDING WHILE IMMersed IN THE MOLTEN METAL. *a*, SURFACE OF THE EMBRITTLED BAR, BENT AFTER REMOVAL FROM THE COPPER. $\times 1$. *b*, SECTION THROUGH A PORTION OF *a*. $\times 100$. NOTE THE INTERCRYSTALLINE PENETRATION OF THE COPPER INTO THE IRON.

cause the trouble, should be localized along the grain boundaries and disseminated as completely as possible. A given amount of oxide distributed in this manner ought to give rise to a much higher degree of brittleness than a similar amount occurring in the form of much fewer but larger particles. The results presented by Miss Leiter have ably demonstrated that this is so.

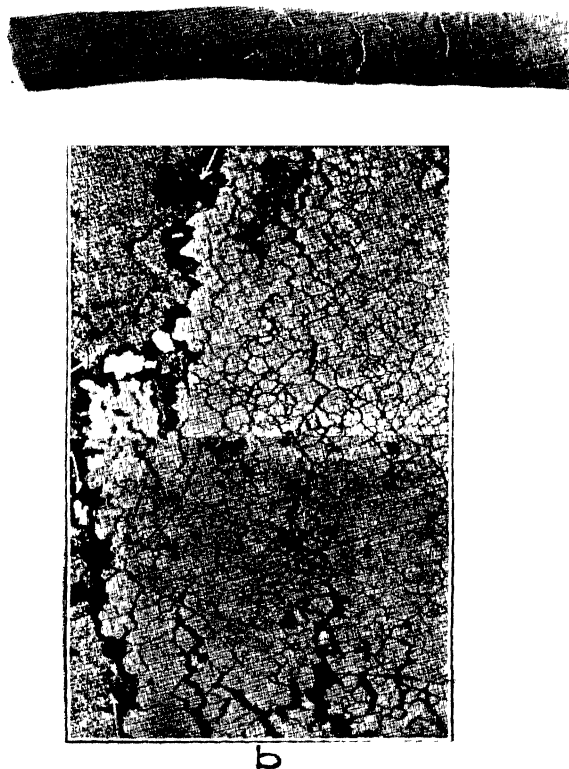


FIG. 6.—INTERCRYSTALLINE BRITTLINESS SHOWN BY NICKEL WHEN STRESSED IN TENSION AT 900° C. *a*, EXTERNAL APPEARANCE OF WIRES USED. $\times 5$. *b*, LONGITUDINAL SECTION THROUGH THE FRACTURED END. $\times 100$ REDUCED TO $\times 50$.

During the past few years, considerable attention has been given at the Bureau of Standards to the problem of intercrystalline brittleness of metals. Reference to a few random examples, illustrating this property of metals may be of interest and will serve to illustrate the point that the embrittlement of copper is best to be regarded as a specific case of the more general problem.

The Bureau was asked to explain why a wrought iron bar used as a stirring rod in a crucible of molten copper became very brittle. Fig. 5 gives the data which furnished the answer. A rod of the iron simply

immersed in molten copper suffered no deterioration other than the loss of a little metal from the surface by solution in the copper. A similar rod, stressed by bending, while immersed in the molten copper became brittle. As shown in Fig. 5, the molten copper penetrated into the interior of the bar along an intercrystalline path. The intercrystalline 'bond,' already weakened by the high temperature, was further weakened by the applied stress. This readily made possible the intercrystalline attack and penetration of the iron by the molten copper.

Oxidation at high temperatures, in some metals, shows a tendency, at least in the initial stage, to follow an intercrystalline path. This is particularly true for nickel. If the strength of intercrystalline "bond" is somewhat lowered by applying a tensile stress, to the heated specimen,

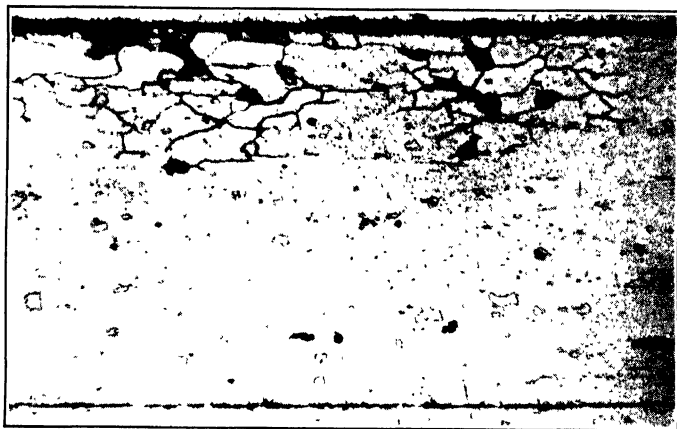


FIG. 7.—LIGHT ALUMINUM ALLOY SHEET SHOWING EMBRITTLEMENT BY INTERCRYSTALLINE CORROSION. $\times 250$. ETCHANT, 10 PER CENT. SODIUM HYDROXIDE. THE MICROGRAPH SHOWS AN ENTIRE SECTION THROUGH THE SHEET.

the oxidation proceeds readily along an intercrystalline course and the metal breaks with the fracture typical of intercrystalline brittleness as is shown in Fig. 6.

Some metals and alloys show, even at ordinary temperatures, a tendency toward intercrystalline oxidation (corrosion). Fig. 7 illustrates this in a thin sheet of one of the light aluminum alloys. Instead of the atmospheric corrosive attack being distributed fairly uniformly over the corroded surface, it was localized and penetrated the interior of the sheet along an intercrystalline course. It is evident that the mechanical properties of the sheet would be affected much more seriously by this type of corrosive attack than by the same degree of corrosion spread uniformly over the surface. Actually, a tension test of this material will show that the ductility of the sheet is very low indeed, as compared to the same material in the uncorroded condition.

Although these three examples may seem quite unrelated to one another and to the case under discussion, they are alike in that they all illustrate a fundamental characteristic of metals, a knowledge of which must be assumed in any discussion of any specific case of intercrystalline brittleness of metals.

[NOTE.—The first two papers on the program of the symposium on “gas” in copper were read before the chairman called for discussion. On this account the discussion from the floor on Mr. Fuller’s paper is presented on page 772.]

Action of Reducing Gases on Heated Copper

BY W. H. BASSETT* AND J. C. BRADLEY,† WATERBURY, CONN.

(New York Meeting, February, 1926)

In considering the effects of reducing gases on hot solid copper the following conclusions have been reached. (1) Depth of deoxidation of copper heated in reducing gas is greater the smaller the amount of cuprous oxide originally present in the copper, the range studied being from 0.015 to 0.136 per cent. oxygen. It is suggested that the reason for this difference in depth of deoxidation is that, when the copper is low in cuprous oxide, the reducing gas is diluted less by the gas that is formed in the reaction than when the copper is high in cuprous oxide; and the greater the concentration of the reducing gas the deeper the deoxidation. (2) The rate of deoxidation is much more rapid at the beginning of exposure than at the end, a condition especially noticeable at temperatures around 900° C.; that is, deoxidation is retarded as the depth penetrated by the reducing gas increases. (3) Within the accuracy of the experiments arsenic in copper up to 0.5 per cent. has no tendency to increase or decrease the action of a reducing gas on the cuprous oxide present in the copper.

IN 1912 pieces of 0.365-in. hard copper rod $\frac{1}{2}$ in. long were heated in a porcelain tube in an electric furnace, while illuminating gas was passed through. An approximate analysis of this gas is:

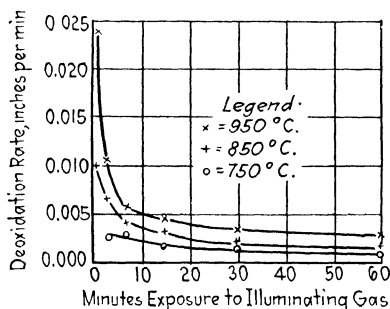


FIG. 1.—EFFECT OF TIME AND TEMPERATURE ON DEOXIDATION RATE OF 0.365-IN. COPPER BY ILLUMINATING GAS; COPPER PLUS SILVER, 99.983 PER CENT.

Hydrogen 38 per cent., carbon monoxide 30 per cent., illuminants 13 per cent., methane 10 per cent., ethane 3 per cent., carbon dioxide 3 per cent., nitrogen 2 per cent., oxygen 0.4 per cent. After heating for various lengths of time at various temperatures, samples were quenched

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† The American Brass Co.

in water, cut in two, crosswise, polished and etched, and put under the microscope. The line of demarkation between the skin of deoxidized copper and the unchanged core was easily seen. Two kinds of copper were used, one, electrolytic, of high purity, 99.983 per cent. copper plus silver; the other, Lake copper, of considerably lower purity, 99.849 per cent. copper plus silver. Tables 1 and 2 and Fig. 1 show the data obtained.

TABLE 1.—*Deoxidation of 0.365-in. Diameter Copper by Illuminating Gas*

Heated at ° C.	Per Cent. Copper + Silver	Time of Exposure to Gas, Minutes								
		Δ*	1	3	7	15	30	60	120	240
		Depth of Deoxidation, in Inches								
550	99.983						0 000	0 002	0 012	0 016
550	99.849						0 000	0 000	0 004	0 005
650	99.983				0 004	0 004	0 017	0 024		
650	99.849				0 000	0 002	0.010	0 011		
750	99.983			0 008	0 018	0 025	0.035	0 069		
750	99.849			0 004	0 006	0.012	0 020	0 054		
850	99.983	0 010	0 020	0 028	0 046	0 052	0 080			
850	99.849	0 006	0 012	0 028	0 032	0 042	0 058			
950	99.983	0 012	0 024	0 032	0 039	0 067	0 097	0 176		
950	99.849	0 008	0.016	0 019	0 025	0 033	0.048	0 066		

* Short time needed to bring temperature to 950° C.

TABLE 2.—*Effect of Time and Temperature on Rate of Deoxidation of 0.365-in. Copper by Illuminating Gas*

Heated at ° C	Per Cent Copper + Silver	Time of Exposure to Gas, Minutes							
		1	3	7	15	30	60	120	240
		Rate of Deoxidation, in Inches per Minute							
550	99.983					0 0000	0 00003	0 00010	0 00007
550	99.849					0 0000	0.0000	0.00003	0 00002
650	99.983			0 0006	0 0003	0 0006	0 0004		
650	99.849			0 0000	0 0001	0.0003	0.0002		
750	99.983		0 0027	0 0026	0 0017	0.0012	0.0011		
750	99.849		0 0013	0.0009	0.0008	0.0007	0.0009		
850	99.983	0 010	0 0067	0.0040	0.0031	0 0017	0.0013		
850	99.849	0.006	0.0040	0.0040	0.0021	0 0014	0 0010		
950	99.983	0 024	0.0107	0 0056	0 0045	0.0032	0.0029		
950	99.849	0.016	0.0063	0.0036	0.0022	0.0016	0.0011		

The data indicate that the rate of deoxidation is very rapid during the early stages of exposure to reducing gases but decreases as time and depth of deoxidation increase. Further, the high purity copper was deoxidized to a greater depth in a given time at a given temperature than the low purity copper.

Other data, obtained in 1912, were on ten samples of various purities of 0.365-in. diameter copper rod; these were heated for $\frac{1}{2}$ hr. at 750° C. in illuminating gas as before. The results are shown in Table 3. All,

TABLE 3.—*Effect of Purity of 0.365-in. Diameter Copper on Deoxidation in Illuminating Gas, at 750° C.*

Mark	Copper and Silver, Per Cent	Depth of Deoxidation, Inch
4	99.983	0.043
10	99.975	0.043
5	99.969	0.043
9	99.964	0.043
6	99.908	0.047
8	99.849	0.047
7	99.895	0.055
2	99.891	0.059
1	99.907	0.063
3	99.855	0.067

except 8 and 3, were electrolytic copper. Oxygen analyses were not made, but the 99.983 per cent. material would carry around 0.015 per cent. oxygen, while the low purity copper might be expected to have about five times this amount.

Tables 4 and 5 give more data on the 0.365-in. copper rods. Samples 3 and 4 were originally 2 $\frac{1}{2}$ B. & S. numbers hard; 8 and 10, 1 B. & S. numbers hard. Some were annealed 1 hr. at 850° C. in a non-reducing atmosphere prior to treatment. For the tests samples $\frac{1}{2}$ in. long were heated in a copper tube while passing in illuminating gas; they were water quenched. Some of the deeply deoxidized specimens were badly shattered.

The data of Table 4 indicate, as might be expected, that there is no difference in the amount of deoxidation whether samples were previously hard or soft, as heating in the reducing atmosphere anneals the hard samples and brings them to the same state as those that were already soft. On the other hand, within the accuracy of the experiment, there is no indication of any material difference in deoxidation whether the samples were high or low in oxygen content. Further evidence on this matter will be given later. Table 5 shows again the marked decrease in rate of deoxidation as time of exposure to gas, and depth of deoxidation increase.

TABLE 4.—*Hard and Soft 0.365-in. Diameter Copper Heated in Illuminating Gas and Quenched*

Temperature, ° C.	Mark	Per Cent. Copper + Silver	Temper	Time of Exposure to Gas, Minutes			
				15	30	60	120
Depth of Deoxidation, Ins.							
550	4	99.983	Soft Hard			0.004 0.004	0.010 0.004
	3	99.975	Soft Hard			0.004 0.004	0.008 0.008
	10	99.855	Soft Hard			0.004 0.004	0.012 0.008
	8	99.849	Soft Hard			0.004 0.004	0.006 0.014
650	4	99.983	Soft Hard	0.016 0.012	0.018 0.012	0.014 0.014	
	3	99.975	Soft Hard	0.008 0.012	0.014 0.012	0.018 0.020	
	10	99.855	Soft Hard	0.012 0.012	0.008 0.014	0.021 0.016	
	8	99.849	Soft Hard	0.012 0.008	0.008 0.010	0.016 0.020	
750	4	99.983	Soft Hard	0.033 0.029	0.024 0.043	0.047 0.067	
	3	99.975	Soft Hard	0.026 0.028	0.035 0.031	0.075 0.059	
	10	99.855	Soft Hard	0.041 0.029	0.028 0.059	0.067 0.030	
	8	99.849	Soft Hard	0.033 0.031	0.037 0.041	0.063 0.067	
850	4	99.983	Soft Hard	0.067 0.055	0.073 0.059	0.071 0.083	
	3	99.975	Soft Hard	0.055 0.055	0.063 0.087	0.086 0.182	
	10	99.855	Soft Hard	0.063 0.047	0.075 0.071	0.087 0.077	
	8	99.849	Soft Hard	0.059 0.051	0.063 0.043	0.095 0.075	
950	4	99.983	Soft Hard	0.083 0.102	0.182 0.182	0.182 0.182	
	3	99.975	Soft Hard	0.098 0.028	0.182 0.125	0.182 0.182	
	10	99.855	Soft Hard	Shattered 0.043	Shattered 0.071	Shattered 0.182	
	8	99.849	Soft	0.067	0.182	Shattered	

TABLE 5.—*Deoxidation of Copper, Data Condensed from Table 4*

Temperature, ° C.	Time of Exposure to Gas, Minutes			
	15	30	60	120
Rate of Deoxidation, Inches per Minute				
550			0.0001	0.0001
650	0.0008	0.0008	0.0003	
750	0.0021	0.0013	0.0009	
850	0.0038	0.0022	0.0014	
950	0.0049	0.0049	0.0030	

EFFECT OF AMOUNT OF OXYGEN ON DEOXIDATION

It has been thought that depth of deoxidation of copper was greater the larger the amount of oxygen;¹ the data already presented in the present paper has been inconclusive on this point. L. P. Webert, in The American Brass Co. Laboratory, has done some work indicating that the opposite is true; and more recently we have confirmed this—that copper with low oxygen content is deoxidized more deeply than copper with higher oxygen content, time, temperature, and kind of gas being identical. Webert showed this in two experiments.

In one case, hot-rolled copper was used. This had an elliptic cross-section with $\frac{1}{2}$ and $1\frac{1}{16}$ -in. axes. The cuprous oxide was more concentrated in that portion which corresponded to the set of the wire bar than elsewhere. Pieces 2 in. long were exposed to reducing gases, for 1 hr., at 840–900° C. Depth of deoxidation was determined under the microscope to be greater where oxygen was low than where the oxygen content was higher. At places where the cuprous oxide was distributed, as in Fig. 2, the depth of deoxidation averaged 0.068 in.; while where the cuprous oxide particles were more numerous, as in Fig. 3, the average depth of deoxidation was only 0.038 in. These photomicrographs show the samples unetched; the black dots represent the cuprous-oxide particles.

The copper-silver content of the wire bars tested was 99.942 and 99.954 per cent. In one case, the gas used analyzed 17.1 per cent. hydrogen, 15.0 per cent. carbon monoxide, and 6.1 per cent. carbon dioxide; in another, it was 26.2 per cent. hydrogen, 19.5 per cent. carbon monoxide, and 4.7 per cent. carbon dioxide. The depth of deoxidation was slightly less in these particular cases, when the copper was exposed to the apparently more reducing gas.

¹ Norman B. Pilling: Action of Reducing Gases on Hot Solid Copper. *Trans.* (1919) **60**, 333.

W. H. Bassett: *Trans.* (1919) **60**, 337.

Moore and Beckinsale: *Jnl. Inst. Metals* (1921) **25**, 233.

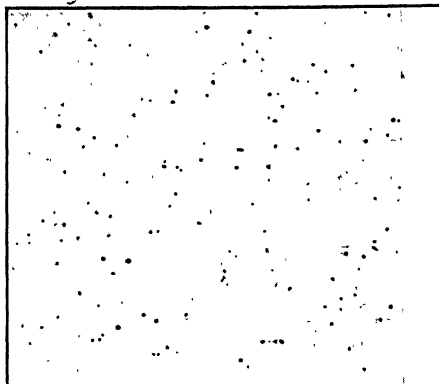


FIG. 2.—WITH Cu_2O PARTICLES FAR APART, DEPTH OF DEOXIDATION OF COPPER WAS 0.068 IN. $\times 75$; NOT ETCHED.

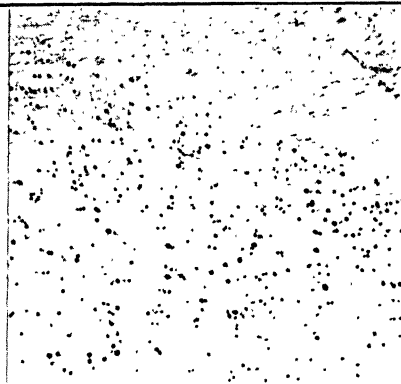


FIG. 3.—WITH Cu_2O PARTICLES CLOSER, DEPTH OF DEOXIDATION WAS 0.038 IN. $\times 75$; NOT ETCHED.

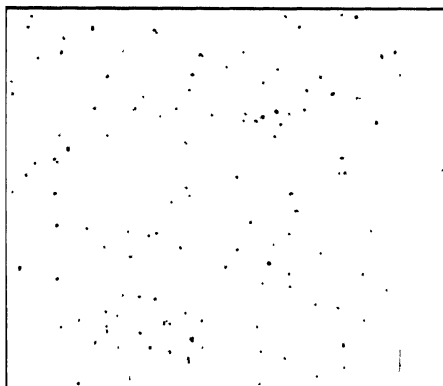


FIG. 4.—OXYGEN, 0.026 PER CENT.

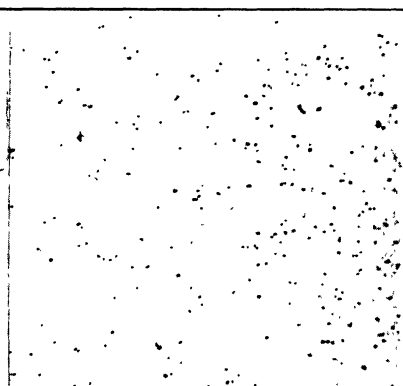


FIG. 5.—OXYGEN, 0.033 PER CENT.

DISTRIBUTION OF OXYGEN IN 0.083-IN. COPPER TUBING. $\times 75$; NOT ETCHED.

FIG. 6.—OXYGEN, 0.046 PER CENT.

FIG. 7.—OXYGEN, 0.073 PER CENT.

DISTRIBUTION OF OXYGEN IN 0.083-IN. COPPER TUBING. $\times 75$; NOT ETCHED.

In another experiment, four copper tubes 1-in. outside diameter with an 0.083-in. wall were used. In each, the cuprous oxide was evenly distributed, as shown by Figs. 4, 5, 6, and 7. Analyses are given in Table 6. The tubes selected formed a series varying in oxygen content. Treatments for 1 hr. were made in gases of various compositions at 800–900° C. For each test four specimens, 2½ in. long, of differing oxygen content, were stood in a row in a gas-fired furnace. At the same time specimens of arsenical sheet copper were exposed, the sheets and tubes being placed alternately, and so bolted together that the distance from specimen to specimen was never less than ⅛ in. Two small perforated pipes distributed air and gas evenly behind a baffle plate in the furnace, so gases would be so thoroughly mixed and suitably deflected as to come as uniformly as possible in contact with all samples. For gas analyses during a given experiment, a sampling tube, also perforated, drew a constant stream of gases from the heating chamber.

TABLE 6.—*Analyses of Copper Tubes Used for Deoxidation Tests*

Sample Number	5	18	3	12
Analysis Number	88131	90750	88129	88138
Figure Number	4	5	6	7
Oxygen, per cent	0 026	0 033	0 046	0.073
Copper, per cent	99 979	99.931	99.956	99 893
Silver, per cent	0 0001	0 0349	0 0021	0.0203
Gold, per cent. . .	0 00001	0.0000	0 00002	Trace
Arsenic, per cent.	0 0011	0.0033	0.0007	0.0056
Antimony, per cent	0 0006	0.0002	0.0010	0.0002
Lead, per cent. . .	0.0005	0.0005	0.0006	0.0011
Tin, per cent. . . .	0.0000	0 0000	0.0000	0.0000
Iron, per cent. . . .	0 0020	0 0016	0.0020	0.0016
Manganese, per cent	0 0000	0 0000	0.0000	0.0000
Nickel, per cent	0 0018	0.0016	0.0017	0.0013
Bismuth, per cent.	0.0000	0.0000	0.0000	0.0000
Zinc, per cent.	0.0000	0.0000	0.0000	0.0000
Selenium and tellurium, per cent	0 0000	0.0000	0.0001	0.0000
Sulfur, per cent	0 0036	0.0037	0.0036	0.0041

The amount of reducing gases in the furnace was adjusted by a valve on the air pipe, the illuminating gas pipe being open all the time. When the reducing gases ran high in the furnace sufficient heat was not supplied to maintain the temperature at 800–900° C.; at such times additional heat was supplied on the outside of the muffle compartment of the furnace. When the reducing gases were low in amount, the muffle had to be cooled on the outside by a blast of air. The deoxidized area was

magnified 100 times and the distance between the inner edge of the tube section and the border of the unreduced oxide portion was measured on the ground glass of the microscope at four points around the circumference of the tube. Table 7 gives the data of these tests.

TABLE 7.—*Deoxidation of .083-in. Copper Tubing*

Temperature Range, ° C.			Gas Analyses				Deoxidation, 1 Hr. Exposure, Inches			
Test	Min.	Max.	H Per Cent.	CO Per Cent.	CO ₂ Per Cent.	O Per Cent.	No. 5 Oxygen 0 026 Per Cent.	No. 18 Oxygen 0 033 Per Cent.	No. 3 Oxygen 0 046 Per Cent.	No. 12 Oxygen 0 073 Per Cent.
1	950	980	0.0	0 0	11.7	0.6	0 000	0 000	0 000	0 000
2	860	870	3.7	4 7	10.8	0.0	0 034	0 028	0 026	0 014
3	820	840	3.9	5 4	8.9	0.0	0 023	0.014		0 000
4	810	820	7.2	8 5	8.4	0 0	0 027	0 017	0.025	0 018
5	820	880	8.1	10.0	7.8	0 0	0 039	0 037	0 025	0 026
6	830	900	8.4	10.4	8.0	0 0	0 028	0 032	0.022	0 017
7	865	870	11.3	10.8	6.9	0.0	0 041	0 031	0 028	0.024
8	820	850	11.7	11.5	6.6	0 0	0 041	0 031	0 029	0 024
9	820	860	17.3	16.0	6.0	0.0	0 042	0 042	0.042	0 038
10	860	900	17.1	15.0	6.1	0 0	0.042	0 042	0 042	0 042
11	840	890	26.2	19.5	4.7	0 0	0 042	0 042	0 042	0 042
Average of Tests Nos. 2 to 8										
	810	900	7.8	8.8	8.2	0 0	0 033	0 027	0 026	0 018

As the tubes were 0.083 in. in diameter, deoxidation given at 0.042 in. means that the tubes were completely deoxidized, being exposed on both inside and outside.

The Less the Oxygen the Deeper the Deoxidation

By averaging results in the seven tests where hydrogen varies from 3.7 to 11.7 per cent. and where deoxidation of tubes proceeded only part way through the samples, it was found that the copper with low oxygen is deoxidized more deeply than that with higher oxygen; *i.e.*, in 1 hr., in gas carrying about 8 per cent. hydrogen, and at a temperature of about 850°C., the depth of deoxidation of copper varied with the oxygen content as follows.

DEOXIDATION, INCH

0.033

0.027

0.026

0.018

OXYGEN, PER CENT.

0.026

0.033

0.046

0.073

To verify these findings, further work has been done when small portions of copper were used, $\frac{5}{8}$ in. long, $\frac{1}{4}$ in. wide, 0.052 to 0.084 in. thick. Some of these were from pieces of 1-in. O. D. tubing, flattened, then filed and smoothed on emery cloth, while others were from cold-rolled sheet copper, also filed and smoothed on fine emery cloth, prior to heat treatment; one was cut from a firebox $1\frac{1}{8}$ in. thick. A small hole was bored in one end of each sample so that they could be assembled on a bolt for microscopical examination of the deoxidized sections, because, held together, the edges of the sections would not be rounded when polished.

For heat treatment, samples were tied together by fine copper wire so that all lay flat side by side and all the broad surfaces were equally exposed to the reducing gas. They were placed in the cold end of a $\frac{3}{8}$ -in. I. D. fused-quartz tube 44 in. long, and commercial gas with 9 per cent. hydrogen and 91 per cent. nitrogen run through. The tube was placed in a 31-in. electric furnace. When at 700°C ., the string of nine samples was pulled into the middle of the hot tube. The furnace was so large, compared with the size of the samples, that the temperature did not change appreciably and samples came up to heat very quickly.

The samples were chosen with a wider variety of oxygen content than before. They were not arranged in the order of oxygen content when heated, but were mixed so high and low oxygen samples would be in close proximity, so as to decrease possible error due to entering gases striking one sample before another. When samples had been heated a certain length of time, the tube was removed from the furnace and cooled quickly with an electric fan, the reducing gas still passing.

ANALYSES OF $\frac{5}{8}$ BY $\frac{1}{4}$ -IN. SAMPLES

The copper reported in Table 8 as carrying 0.004 per cent. oxygen was deoxidized with phosphorus when cast. Oxide was not present as Cu_2O , as determined by microscopical examination. No harm came to this copper in the presence of the reducing gases, while the others were rendered brittle to various depths, as revealed by the microscope.

TABLE 8.—*Analyses of $\frac{5}{8}$ by $\frac{1}{4}$ -in. Copper Used in Experiment*

Analysis Number.....	90726	6353	88131	88132	2561	88130	6356	91361	5087
Sample Number	24	10	5	6	8	4	12	0	26
From.....	Tube	Sheet	Tube	Tube	Sheet	Tube	Sheet	Fire-box	Sheet
Oxygen, per cent	0 004	0 015	0 026	0 044	0 071	0 077	0 080	0 090	0 136
Copper, per cent	99 975	99 953	99 979	99 949	99 560	99 926	99 356	99 404	99 855
Silver, per cent	0 0024	0 0242	0 0001	0 0005	0 0948	0 0027	0 0225	0 0828	0 0005
Gold, per cent	0 00004	0 00001	0 00001	0 00001		0 00003			
Arsenic, per cent	0 0001	0 0025	0 0011	0 0001	0 2691	0 0001	0 5361	0 400	0 0012
Antimony, per cent	0 0003	0 0008	0 0006	0 0003	0 0000	0 0002	0 0004	0 0002	0 0002
Lead, per cent.....	0 0007	0 0008	0 0005	0 0003	0 0011	0 0009	0 0023	0 000	0 0016
Tin, per cent	0 0000		0 0000	0 0000		0 0000			
Iron, per cent.....	0 0057	0 0025	0 0020	0 0019	0 0003	0 0022	0 0008	0 0013	0 0015
Manganese, per cent	0 0005		0 0000	0 0000		0 0000			
Nickel, per cent	0 0034	0 0000	0 0018	0 0011	0 0018	0 0011	0 0014	0 0052	0 0012
Bismuth, per cent	0 0000		0 0000	0 0000		0 0000		0 000	
Zinc, per cent	0 0024	trace	0 0000	0 0000	0 0000	0 0000	0 0000		0 0000
Selenium and tellurium, per cent	0 0000		0 0000	0 0000		0 0000		0 0008	0 0000
Sulfur, per cent	0 0048	0 0011	0 0036	0 0047	0 0022	0 0042	0 0014	0 0032	0 0032
Phosphorus, per cent	0 0004								

The quantity of hydrogen passed over the samples was 80 to 120 times more than the amount corresponding to the copper oxide reduced; data bearing on this point are shown in Table 9.

TABLE 9.—*Quantity of Hydrogen Used in Experiment on $\frac{5}{8}$ by $\frac{1}{4}$ -in. Copper Samples*

Temperature, ° C.	Time of Run, Minutes	9 Per Cent Hydrogen Used, Liters	Weight of Hydro- gen Alone, Milli- grams	Hydrogen Equiva- lent to Cu_2O Re- duced, Milligrams (Approx.)
700	5	1½	12	0 14
700	15	5	40	0 34
700	25	5	40	0 50

TABLE 10.—*Deoxidation of $\frac{5}{8}$ by $\frac{1}{4}$ -in. Copper with Various Amounts of Oxygen (and Arsenic)*

Sample No.	Per Cent Oxygen	Per Cent. Arsenic	Depth of Deoxidation of Copper Exposed to 9 Per Cent. Hydrogen (91 Per Cent Nitrogen) at 700° C. for Lengths of Time Noted, Inch		
			5 Min.	15 Min	25 Min.
24	0.004	0 0001			
10	0.015	0.0025	0 007	0.017	0.021
5	0 026	0.0011	0.006	0.016	0.024
6	0 044	0 0001	0.006	0 017	0.027
8	0.071	0 2691	0.005	0.010	0.015
4	0.077	0.0001	0.005	0.013	0.017
12	0.080	0.5361	0.007	0.015	0.020
0	0.090	0.400	0.004	0.007	0.011
26	0.136	0.0012	0.006	0.011	0 015
Ave.	0.060		0.0056	0.0133	0.0187

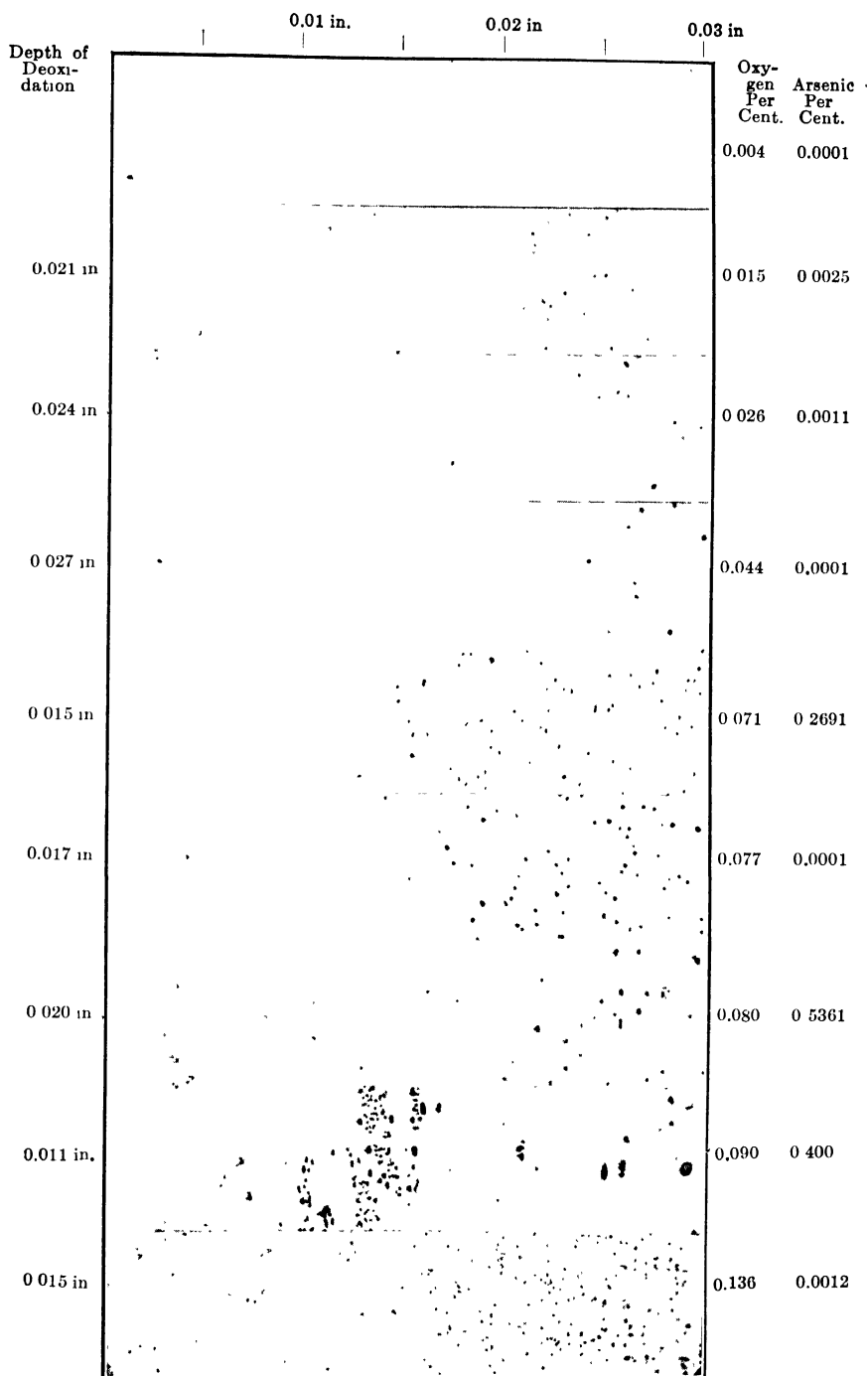


FIG. 8.—DEPTH OF DEOXIDATION OF COPPER IN 9 PER CENT. HYDROGEN GAS AT 700° C. FOR 25 MIN. $\times 100$; NOT ETCHED.

Photomicrographs of samples heated for 25 min. are shown in Fig. 8. These are arranged according to original oxygen content and, in a general way, indicate decrease in depth of deoxidation as per cent. of oxygen increases. They also show the considerable variation in size and concentration of cuprous-oxide particles present in the various coppers tested. The right-hand portions of the photomicrographs show the unreduced cuprous-oxide particles; the left-hand portions show depth of deoxidation and absence of cuprous oxide. Samples were not etched.

The data of Table 10 have been plotted in Fig. 9. The points do not lie on a very regular curve, but it is thought that they bear out the previous findings and indicate again that for a given time, temperature, and gas, the depth of deoxidation of copper is greater the smaller the

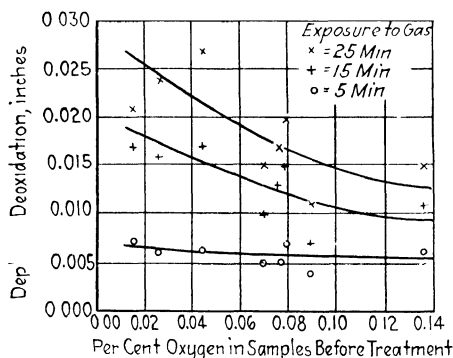


FIG. 9.—EFFECT OF OXYGEN CONTENT ON DEPTH OF DEOXIDATION OF COPPER EXPOSED FOR VARIOUS LENGTHS OF TIME TO GAS WITH 9 PER CENT. HYDROGEN AT 700° C.

amount of cuprous oxide originally present. The copper carrying as little as 0.015 per cent. oxygen, when bent double, had a characteristic brittle break.

The more oxide there is present the more hydrogen is used in the reaction, and the less there is to penetrate further; in consequence, the depth of deoxidation is not as great. Furthermore, the penetration of hydrogen into the copper is increasingly hindered by the formation of steam, for steam does not diffuse through copper as fast as hydrogen,² and therefore cannot get out as fast as it forms. Pilling has found³ that the speed at which hydrogen diffuses into copper varies greatly with the external hydrogen concentration. There seems to be no reason why this should not apply to internal concentration of hydrogen in the copper; that is, the steam formed in the copper, and the exhaustion of hydrogen by reaction with cuprous oxide, decrease the hydrogen concentration, retarding its penetration and its further reduction of the oxide.

² Norman B. Pilling. *Trans.* (1919) 60, 327.

³ *Jnl. Inst. Metals* (1921) 25, 255.

RETARDATION OF RATE OF DEOXIDATION WITH INCREASE OF TIME

That the reaction is slowed up as depth of deoxidation increases is shown by Table 11, which gives, in condensed form, data from Table 10; these figures show that the retardation of the rate of deoxidation, with increase of time of exposure to a reducing gas, is considerable.

TABLE 11.—*Retardation of Rate of Deoxidation with Time of Exposure*

Time of Exposure to 9 Per Cent Hydrogen at 700° C., Minutes	Depth of Deoxidation Average of 8 Samples from Table 10, Inch	Rate of Deoxidation, Inches per Minute
5	0.0056	0 00112
15	0.0133	0.00089
25	0 0187	0 00075

Similar data were given in Table 2 and plotted in Fig. 1, where it is shown that retardation of rate of deoxidation with time is much more pronounced at 950° C. than at 700°, the temperature of Table 11.

Pilling⁴ noted not only that the rate of diffusion through copper varied enormously with the external hydrogen concentration but that the curve of variation consisted of two well-defined branches. His data indicate that, below 28 per cent. hydrogen concentration, the time of exposure was 1 hr., while at 48 per cent., the copper was exposed for only 30 min., and with 100 per cent. hydrogen for only 10 min. Probably the curve would have been a simple one if the time of exposure to the gases had been the same in all cases, for, as found above, the rate of deoxidation decreases as the time of exposure and depth of deoxidation increase. On the other hand, it would not be expected that the curve would be a straight line, because, as the external hydrogen concentration and depth of deoxidation increase, the effective internal hydrogen concentration lags coincidentally with the increasing concentration of water vapor.

The foregoing may explain our findings that copper with low oxygen is deoxidized more deeply in hydrogen than copper with higher oxygen; for the amount of water vapor formed in the copper decreases with a decrease in oxygen content; and this small quantity of water vapor dilutes the incoming hydrogen less than the larger quantities of water vapor formed in copper with higher oxygen.

EFFECT OF ARSENIC ON DEOXIDATION OF COPPER

Some arsenical coppers analyzed, as shown in Table 12, were exposed for 1 hr. to reducing gases at the same time as those shown in Table 7. All had been hot rolled to 0.183 in.; the first two were then cold rolled to 0.050 in., and the last three to 0.083 in.

⁴ *Jnl. Inst. of Metals* (1921) 25, 255.

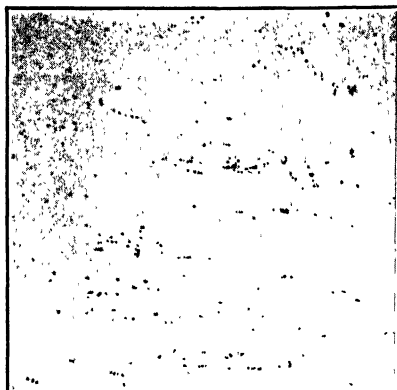


FIG. 10.—ARSENIC, 0.044 PER CENT.; BEFORE GASSING, SHOWS Cu_2O . $\times 75$; NOT ETCHED.



FIG. 11.—ARSENIC, 0.044 PER CENT.; AFTER GASSING, CRACKED. $\times 75$; ETCHED.

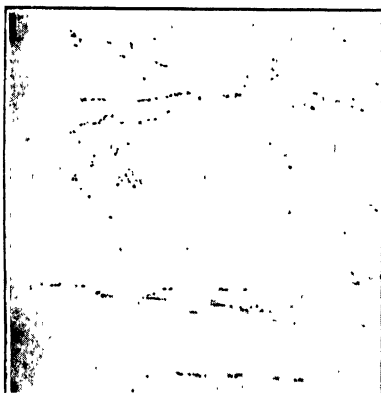


FIG. 12.—ARSENIC, 0.079 PER CENT.; BEFORE GASSING, SHOWS Cu_2O . $\times 75$; NOT ETCHED.



FIG. 13.—ARSENIC, 0.079 PER CENT.; AFTER GASSING, CRACKED. $\times 75$; ETCHED.

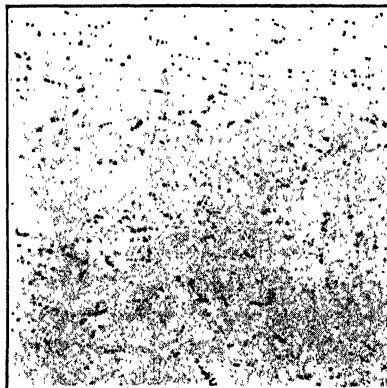


FIG. 14.—ARSENIC, 0.100 PER CENT.; BEFORE GASSING, SHOWS Cu_2O . $\times 75$; NOT ETCHED.

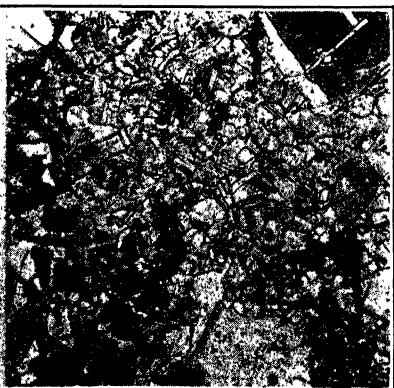


FIG. 15.—ARSENIC, 0.100 PER CENT.; AFTER GASSING, CRACKED. $\times 75$; ETCHED.

TABLE 12.—*Arsenical Copper Analyses*

Analysis	Copper, Per Cent.	Arsenic, Per Cent.	Iron, Per Cent	Oxygen, Per Cent. (estimated) ^a
		0 044		0.025
		0 079		0.025
17621	99 788	0 100	0 009	0.030
17622	99 638	0 281	0 003	0 030
17623	99 519	0 413	0 002	0 00

^a Estimated roughly by comparison with photomicrographs of coppers of known oxygen content.

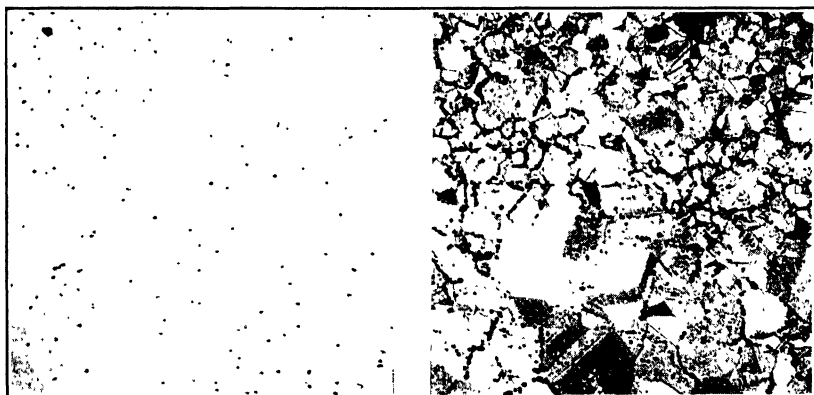


FIG. 16.—ARSENIC, 0.281 PER CENT.; BEFORE GASSING, SHOWS Cu_2O . $\times 75$; NOT ETCHED.

FIG. 17.—ARSENIC, 0.281 PER CENT.; AFTER GASSING, CRACKED. $\times 75$; ETCHED.

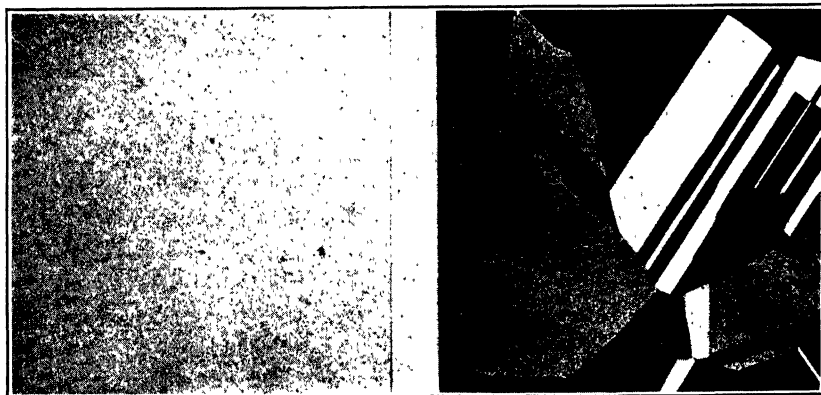


FIG. 18.—ARSENIC, 0.413 PER CENT.; BEFORE GASSING, NO Cu_2O . $\times 75$; NOT ETCHED.

FIG. 19.—ARSENIC, 0.413 PER CENT.; AFTER GASSING, NO CRACKS. $\times 75$; ETCHED.

GASSING OF ARSENICAL COPPERS.

The amount of oxygen present is indicated by Figs. 10, 12, 14, 16, and 18 to be 0.025 to 0.030 per cent. in the first four samples, but nil in the fifth sample. Bending tests, microscopical examination, and Figs. 11, 13, 15, 17, and 19, taken after exposure to the reducing gases, prove that all the metal had been badly embrittled, except the one with no oxygen.

Other data on deoxidation of arsenical copper were included in Table 10; complete chemical analyses were given in Table 8. For some unknown reason all three of these arsenical coppers were considerably off the curve of the coppers that carried practically no arsenic. The arsenic-bearing coppers are plotted at 0.071, 0.080, and 0.090 per cent. oxygen in Fig. 9. The 0.080 per cent. oxygen sample with 0.5361 per cent. arsenic, consistently, at 5, 15 and 25 min. exposure, deoxidized more rapidly than the non-arsenical coppers with nearly the same oxygen; the other two arsenical coppers, however, with 0.2691 and 0.400 per cent. arsenic consistently deoxidized less rapidly than the non-arsenical coppers with nearly the same oxygen content. Within the accuracy of our experiments, the arsenic itself has no tendency to either increase or decrease the action of reducing gases on the cuprous oxide that may be present in the copper.

DISCUSSION

C. S. SMITH, Cambridge, Mass. (written discussion).—The action of reducing gases on copper containing oxygen is a matter of both scientific and practical importance, and it is gratifying to see that it is at last receiving the attention that it deserves.

It is unfortunate that the present paper only deals with the penetration of reducing gases into copper, for, although this may be greater in low-oxygen metal than in high, it is very probable that the violence of the action and the extent of the deterioration would be greater as the amount of oxygen increased—at all events at intermediate temperatures (about 650 to 850° C.).

I have plotted the results given by the authors in the 60-min. column of Table 1 (see Fig. 20). This shows the relation between penetration and temperature, and indicates clearly that the relative difference in the depth of deoxidation is much greater at high temperatures than low. Both the curves show a slight submerged maximum at 750° C., but above this the high-oxygen curve remains practically horizontal, while the other indicates a rapid increase in penetration. If the sole reason for the difference in thickness of the deoxidized layers is the diffusion of the hydrogen and water vapor one would expect that both curves would be similar in form, and that both would rise rapidly and in a regular way with rising temperature. It is evident, therefore, that there is some action which takes place to a greater extent in the high oxygen copper, and

which tends to *reduce* the depth of deoxidation as the temperature increases. I have recently carried out tests on large samples of cast copper which bear this out conclusively. In one case the penetration at high temperature was only one-third of that at 800° C., and in every case a very marked maximum was found at this temperature if the oxygen content of the copper was reasonably high. Low oxygen did not show this phenomenon, and if high-oxygen copper were forged, the effect was very much reduced, the curves being similar to the lower one on Fig. 20.

Mechanical tests on copper wire with about 0.03 per cent. oxygen have shown that metal which has been deoxidized completely at high temperatures is much stronger and less brittle than that which has been treated at intermediate temperatures. There is undoubtedly some connection between this and the other unexpected high temperature effect, and I have

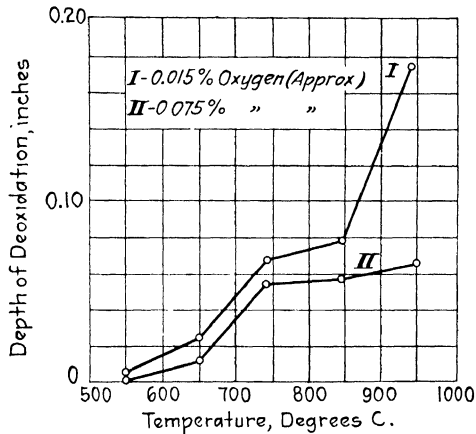


FIG. 20.—CURVE SHOWING THE EFFECT OF TEMPERATURE ON THE DEPTH OF PENETRATION OF REDUCING GAS INTO COPPER (PLOTTED FROM FIGURES GIVEN BY BASSETT AND BRADLEY).

been able to develop a theory which explains satisfactorily all the observed facts. I have also succeeded in completely restoring good properties to copper which had been ruined by gassing, making it very nearly as strong and ductile as it was before treatment.

Owing to the fact that this work is being done in fulfillment of the requirements for an advanced degree at Massachusetts Institute of Technology, I regret that it is not possible for me to give further details at this time, but it is hoped that the work will be available for publication in the course of a few months.

J. L. CHRISTIE, Bridgeport, Conn.—We should impress upon all users of copper that they should specify deoxidized copper when it is necessary. I had an experience with a batch of “tough-pitch” copper tubes bought in the open market. They were silver-soldered over steel rods swaged down, and finally drawn into copper-clad wire. The anneals between

draws were made in an atmosphere of hydrogen. The copper blistered and peeled from the steel during drawing. The cause of the trouble was simple. The concern had been using deoxidized copper, and when they bought some that had not been deoxidized they ran into difficulties.

F. W. HARRIS, Baltimore, Md.—Mr. Fuller's paper¹ serves a very useful purpose to the manufacturer of copper products in illustrating how susceptible copper is to the pernicious influence of reducing gases in the annealing furnace.

An interesting example which came to my notice recently was a piece of $\frac{1}{2}$ -in. copper rod, rolled and drawn from electro-refined wire bar copper of normal oxygen content. The rod had been annealed, and in some unaccountable way had been badly "gassed." The gassing had caused severe embrittlement about halfway through the rod, leaving a normal ductile core, capable of withstanding an elongation of possibly 50 per cent. of its original length without fracture. The outer shell, however, was so brittle that on attempting to bend the rod in the jaws of a vise it broke away clean, leaving a sharply demarcated line of cleavage between the core and the shell.

As often happens in such cases, the producer of the wire bar was blamed for supplying faulty material, whereas it was obvious at once the faulty fabrication was to blame, and a little deeper inquiry on the manufacturer's part would have shown that the trouble lay at his own door.

Mr. Fuller's examples, therefore, in showing the dangers involved in faulty treatment, help both manufacturer and producer alike.

S. SKOWRONSKI, Perth Amboy, N. J.—Many of the complaints that the refineries receive on copper are due, undoubtedly, to the working of the copper in reducing gases. There have been cases where the copper annealing has produced blisters, and those blisters can generally be traced back to the metal having been heated in a reducing atmosphere, forming water vapor and causing blisters. If the refinery could produce oxygen-free copper or copper free from oxygen to a much greater degree than is the case today, it would help materially. But our cheap copper of today is dependent upon large-scale production. If oxygen-free copper is ever produced commercially, I do not believe it will be at the present price.

N. B. PILLING, Bayonne, N. J.—Relative to the enameled wire that was going through Mr. Fuller's furnace at 430° C.: At that temperature you can take large sections of copper and expose them to hydrogen for a long time without injurious action. I am wondering what the condition is in his case that makes the action so extremely rapid. I know of a

¹ See page 744. The first two papers on the program of the symposium on "gas" in copper, were read before the chairman called for discussion.

bright annealing furnace for spooled copper wire which runs at 350 or 375° C., with an atmosphere of natural gas previously cleaned by passing through a cracking furnace. The wire remains in it a good many hours and comes out bright and entirely softened, yet with no indications of the development of brittleness.

T. S. FULLER.—The factors, in addition to the reducing atmosphere, contributing to embrittlement are time, temperature and size of wire. Forty-eight hours in an atmosphere of hydrogen are required to produce appreciable embrittlement in 10 mil. wire at 300° C. Each 25 or 50° rise in temperature above that point cuts down markedly the time required for embrittlement. I do not think that there are any unusual conditions in the enamelling furnace. It so happens that 430° C. is a temperature sufficient to cause the embrittlement of a wire 0.003 in. in diameter in a reducing atmosphere in a very short time.

What Mr. Rawdon says about the grain boundary effect is true, but it must be remembered that in addition, the position of the grain boundaries change as evidenced by the photomicrographs comprising Figs. 1 and 2 in my paper.

In his written discussion Mr. Smith has mentioned that at very high temperatures he does not find the increased embrittlement which he would expect. The reason, I think, is because the fissures which are opened during embrittlement are healed again at very high temperatures by diffusion.

W. C. SMITH, Baltimore, Md.—In connection with some recent work, Mr. Harris has found he could coalesce the oxygen at from 1600° F. upward. The rate of coalescence was increased with the temperature.

Micrographs show a rather peculiar thing: that as the temperature came up reasonably close to the melting point, the cuprous oxide and possibly cuprous sulfide on the grain borders were coalesced into aggregations, and at extremely high temperatures a series of blow holes or gas cavities developed. These can be traced in the micrographs to further enlargement. It seemed as though a reaction had taken place between Cu_2S and Cu_2C at temperatures below the melting point of copper.

It is a little premature to make any definite statement relative to the effect of coalescing a bar at too hot a temperature. Such experiments as we have made indicate that the coalescence of the copper oxide into large globules, followed by rolling, will produce a structure which has rather large-banded masses of copper oxide, and, so far as we have gone, the tensile strength or the physical properties are lower than the copper would have been if it had not been coalesced.

S. SKOWRONSKI.—Have you observed any cracking?

W. C. Smith.—We do not know.

S. SKOWRONSKI.—Coalescing is simply the breaking up of eutectic, going back into primary copper and leaving the oxide behind. We are talking now on the coalescing of the eutectic on a wire bar or on a cake copper.

Johnson published some work on coalescing in 1917 in the *Proceedings* of the Society of Chemical Industry and in the paper which I quoted at the beginning of the meeting, he speaks as follows on the subject of coalescing:

The copper-cuprous oxide eutectic exists as sheaths around the crystals of copper and, although these sheaths become broken up by coalescence of cuprous oxide—resulting from annealing—and by mechanical treatment, the grains of cuprous oxide always remain, and their bad influence upon malleability increases with their number. Rolled sheet, drawn tube and wire, when examined under the microscope, often show parallel trains—erstwhile eutectic sheaths—of cuprous oxide globules, which have been elongated by the rolling or drawing operations. Thus, composite, oxide-rich bands alternate with bands relatively free from oxide.

Cuprous oxide globules, whilst serving as germinative nuclei and promoting earlier recrystallization in their immediate neighborhood at the commencement when cold-worked copper is annealed, actually retard crystal growth subsequently. This retardation is less marked, the higher the state of aggregation of the oxide particles. The greater the number of annealing operations, the coarser become the oxide particles, and the more uniform becomes the crystal grain size in consequence.

The importance of coalescence, as I see it, is that we know that minute traces of impurity affect our annealing. That has been brought out very forcibly this morning. But we do not know whether those same minute traces of impurities will affect coalescence. In other words, if you take two wire bars, side by side, of very minute difference in composition, one of those bars will coalesce to the cuprous oxide state much quicker than the other bar and will give different characteristics in rolling.

C. H. MATHEWSON, New Haven, Conn.—We have made some examinations of samples of copper which, when rolled and polished for engravers' plates, showed various surface defects. We did not get much further than to determine that those surface defects were very closely related to the distribution of oxide in the copper, and it seemed to us that in order to roll copper to produce a sheet which would not show surface defects when polished, it would be necessary to have the oxide very low and quite evenly distributed.

I note that the authors of one of the previous papers state that the arsenical coppers are apparently "gassed" as readily as the nonarsenical coppers. That is in conflict with evidence which I published some years ago in a paper in which comparisons were made between physical properties, including comparisons between arsenical and electrolytic copper. We carried on some treatments in reducing gases, and it certainly appeared that the arsenical copper was more resistant to this form of deterioration. At that time I attributed this to the fact that the arsenical

copper shows its oxygen in the form of larger globules; in fact, the cast arsenical coppers do not, under ordinary circumstances, show anything that may be properly called eutectic. The arsenic causes the copper to coarsen, which undoubtedly must occasion a good many alterations in properties.

I have no very well-defined ideas to what sort of variations in properties one would expect where the particle size of the copper oxide varies as in this case. We are not dealing with the very minute particles which are known to be so effective in hardening metal. Doubtless for some purposes a small number of large oxide particles in copper is preferable to a large number of small particles, while in other cases the same amount of oxide in the form of smaller particles may be more acceptable.

Annealing of Commercial Copper to Prevent Embrittlement by Reducing Gases

BY SUSAN B. LEITER, SCHENECTADY, N. Y.

(New York Meeting, February, 1926)

THAT oxygen in copper has been a source of trouble is well known and that that trouble has been real in the commercial world has been shown by Fuller.¹ Moore and Beckinsale's paper² at the annual meeting of the Institute of Metals in London, 1921, called forth considerable discussion. Prof. T. Turner expressed the opinion that it was not necessary to have cuprous oxide present in sufficiently large quantities to form either globules or seams in order to produce a bad effect if the copper were gassed. This brought up the question of the solubility of oxygen in copper and the authors desired to know whether there were any evidence of such solubility, because their experience was that whenever there was any oxygen in copper it was present in the form of free cuprous oxide, which was practically always in the form of globules. Later Hanson, Marryat, and Ford³ stated that for all practical purposes cuprous oxide may be regarded as insoluble in copper. However, they found particles of the eutectic to coalesce to form much larger particles. They suggested that cuprous oxide was actually slightly soluble in copper, for it was difficult otherwise to understand the mechanism by which such coalescence could take place. W. E. Ruder, in discussing that paper, said that his experiments had led him to conclude that a slight solubility must exist to allow for the ready coalescence of oxide particles, but conductivity tests convinced him that that solubility was very small. Nevertheless, there appeared to be a state of admixture of oxide with copper that closely resembled a colloidal mixture which at first was mistaken for a true solution and which usually existed at the grain boundaries.

The purpose of this paper is to give the results of some investigations, begun in September, 1921, which would seem to show that although cuprous oxide may be only slightly soluble: (1) this solubility is sufficient

¹ T. S. Fuller: Some Examples of Copper Made Brittle by Hot Reducing Gases. Issued as Paper No. 1514-E, with MINING AND METALLURGY, February, 1926.

² H. Moore and S. Beckinsale: Action of Reducing Gases on Heated Copper. *Jnl. Inst. of Metals* (1921) **25**, 219.

³ Investigation of Impurities on Copper. Part 1. The Effect of Oxygen on Copper. *Jnl. Inst. of Metals* (1923) **30**, No. 2.

to allow the coalescence of the cuprous oxide globules as shown by Hanson, Marryat, and Ford and also by F. Johnson,⁴ and (2) that by the proper annealing of the copper, the cuprous oxide that exists at the grain



FIG. 1.—COPPER-CUPROUS OXIDE EUTECTIC. $\times 200$.

FIG. 2.—COPPER-CUPROUS OXIDE EUTECTIC FIRED IN HYDROGEN AT 800°C . $\frac{1}{2}$ HR.

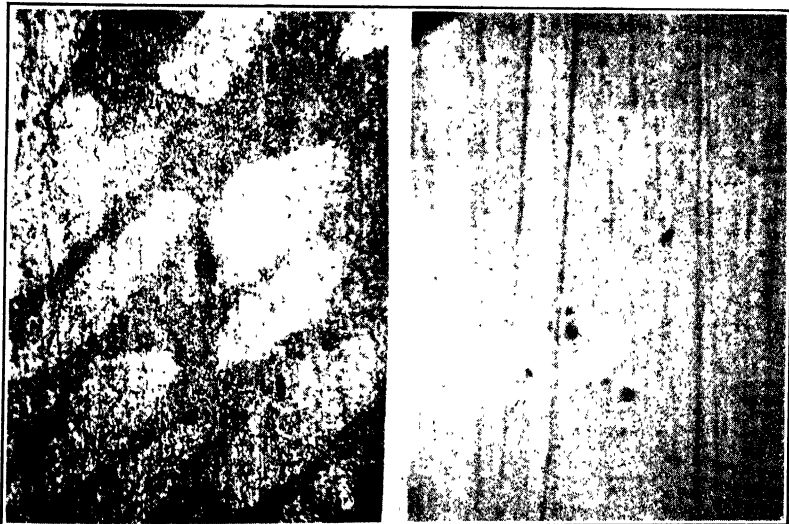


FIG. 3.—COPPER CONTAINING CONSIDERABLE CUPROUS OXIDE SUPERHEATED IN AIR AND QUENCHED. $\times 200$.

FIG. 4.—SAME COPPER AS IN FIG. 3 SUPERHEATED AGAIN AND COOLED SLOWLY. $\times 200$.

boundaries in solid solution or in a finely divided state can be brought together into larger globules and when so coalesced its reduction by hot reducing gases does not cause embrittlement.

⁴ Electrolytic Copper. *Jnl. Soc. of Chem. Ind.* (July 31, 1917).



FIG. 5.—ORDINARY COMMERCIAL COPPER CONTAINING CUPROUS OXIDE IN SCATTERED GLOBULES SUPERHEATED AND QUENCHED; ETCHED WITH PICRIC AND HYDROCHLORIC ACID. $\times 200$.



FIG. 6.—SAME COPPER AS IN FIG. 5 FIRED IN HYDROGEN AT 800°C . $\times 200$.

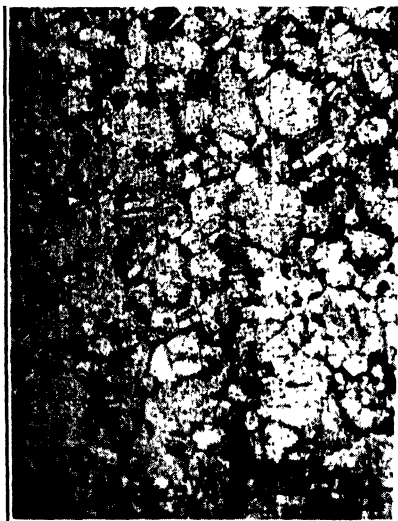


FIG. 7.—COMMERCIAL COPPER HEATED IN HYDROGEN AT 800°C . $\times 200$.



FIG. 8.—COMMERCIAL COPPER GIVEN SPECIAL 900°C . ANNEAL AND AFTERWARD FIRED IN HYDROGEN AT 800°C . $\times 200$.

When the work began the author knew of no etching reagent that would reveal oxygen in solution in copper. The first thing necessary was



FIG. 9.—COPPER CONTAINING 0.055 PER CENT. OXYGEN, UNTREATED; AS POLISHED. $\times 200$.

FIG. 10.—SAME COPPER ANNEALED IN NEUTRAL ATMOSPHERE AT 900°C . $\times 200$.



FIG. 11.—COPPER CONTAINING 0.055 PER CENT. OXYGEN ANNEALED IN NEUTRAL ATMOSPHERE AT 900°C .; FIRED IN HYDROGEN; AS POLISHED. $\times 200$.

FIG. 12.—SAME COPPER FIRED IN HYDROGEN; ETCHED. $\times 200$.

to try to find such a reagent. A sample of copper free from oxygen was subjected to oxygenation until a section was found to contain large

of cuprous-oxide eutectic, Fig. 1. This sample was heated to just above the melting point of copper and quenched; a portion of it, fired in hydrogen at 800° C., cracked open, as shown in Fig. 2. Another portion was carefully polished and used to test various etching reagents. Finally a solution of 50 per cent. of 5 per cent. picric acid in alcohol and 50 per cent. of a 10 per cent. solution of HCl in alcohol gave the appearance of solid solution shown in Fig. 3. When this sample was again superheated and allowed to cool very slowly the grey oxide globules reappeared, Fig. 4.

A sample of ordinary commercial copper containing oxide in scattered globules was superheated and quenched from the molten state. A darkened area was revealed along the grain boundaries, as shown in Fig. 5.



FIG. 13.—COPPER-CUPROUS OXIDE EUTECTIC; AS POLISHED. $\times 200$.



FIG. 14.—SAME COPPER HELD AT 900° C. $\frac{3}{4}$ HR. AND COOLED VERY SLOWLY. $\times 200$.

Fig. 6 shows this same sample with cracks around the grain boundaries after firing in hydrogen.

Under high magnification, the darkened boundary along the grains in Fig. 4 appeared more like a mixture of finely divided cuprous oxide and copper; this observation suggested the theory that there might be in all commercial copper, or copper not oxygen free, thin films between the grains or very narrow grain boundaries of this mixture of cuprous oxide and copper. An attempt was made to collect the oxide so held into larger globules with no connecting film between. Several samples of 100-mil copper wire taken from stock were fired in a neutral atmosphere at various temperatures from 300° to 900° C. and cooled very slowly.

These samples, together with samples of untreated wire, were fired in hydrogen at 850° C. for $\frac{1}{2}$ hr. When tested, all were very brittle except the ones that had been annealed at 900° C. By "very brittle" is meant they broke at the first right-angle bend, while those previously annealed at 900° C. stood six bends without breaking. This has been tested on various sizes of copper wire and copper rods with the same result, if the heating device is such that absolutely no air is allowed to come in contact with the copper during the first part of the drop in temperature from 900° C. The rate of cooling must be very slow. For example, with 100 mil. wire $\frac{1}{2}$ hr. was allowed for the cooling from 900° to 875° C. After that the current was cut off and the copper allowed to cool with the furnace. The microscopic examination of cross-sections of wires checked with the brittleness test. Fig. 7 shows the cracks around the grains where the oxide had been reduced, while in Fig. 8 the grain boundaries are clean

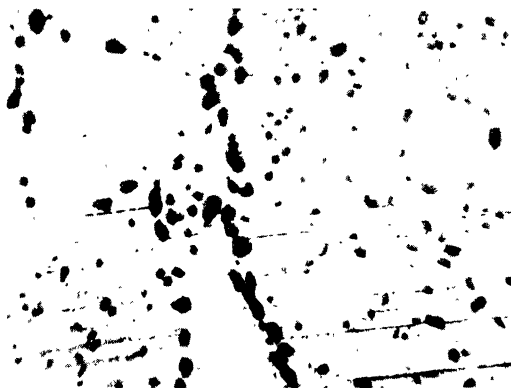


FIG. 15.—SAME COPPER HELD AT 1000° C. $\frac{3}{4}$ HR. AND COOLED VERY SLOWLY. $\times 200$.

and tight, although there are small dark spots showing where oxide globules have been reduced.

The earlier annealing was all done in small electrical furnaces. The samples were placed in copper tubes that were then tightly plugged. These copper tubes were enclosed in heavier walled iron tubes to keep the copper tubes from oxidizing and also to contribute to a slower rate of cooling. No success was attained when the copper tube was exposed to an oxidizing atmosphere during the cooling.

Later, the copper was enclosed in a glass bulb in an atmosphere of nitrogen and heated in a high-frequency furnace. The copper so annealed was ductile after being heated in a reducing atmosphere but the difficulty of regulating the temperature, especially the slow drop from 900° C., made this method impractical. Various methods of covering the copper with dry clean sand or alumina during the anneal were tried; none gave satisfactory results. Copper seems the only metal that can

be used as a container during the anneal without the risk of some reducing effect and consequent embrittlement.

The oxygen content of some of the copper samples was:

Sample 1, 40-mil wire, 0.026 per cent. oxygen

Sample 2, 80-mil wire, 0.064 per cent. oxygen

Sample 3, 124-mil wire, 0.055 per cent. oxygen

Sample 4, $\frac{1}{4}$ -in. rod, 0.039 per cent. oxygen

There was a slight decrease in oxygen after the anneal but the microscopic examination showed the oxide globules still present.

Fig. 9 shows a section of the untreated wire as polished; Fig. 10 gives this same wire after the 900° anneal. The oxide globules appear to be slightly larger and there is a general clearing up of the matrix. Figs. 11 and 12 show the treated wire after it was fired in hydrogen. The small dark spots show where the oxide has been reduced, but the grain boundaries, as will be seen in the etched section, are fine and there is no evidence of cracking.

CONCLUSION

The main cause of the embrittlement of ordinary commercial copper is the reduction of cuprous oxide, which exists either in solid solution or in a finely divided state along the grain boundaries.

By proper annealing, this oxide may be segregated so that its reduction by hot reducing gases will not cause embrittlement.

Three photomicrographs indicating the progress of the coalescence of the cuprous oxide are shown.

The author is indebted to Mr. S. Skowronski for the chemical analysis in connection with this investigation.

DISCUSSION

G. P. HALLIWELL, East Pittsburgh, Pa.—Miss Leiter says that beneficial results could be obtained only when a copper tube was used as the annealing chamber. I wonder if some other material, such as quartz could not be used.

In an effort to check Miss Leiter's results, I annealed some copper strap—ordinary commercial copper with an oxygen content of about 0.05 per cent.—in vacuum, using a procedure as near as possible to that of Miss Leiter's patent, except that I used a quartz tube. Similar metal was also annealed at 725° C. for 1 hr. Samples (7) from each of these lots were thoroughly gassed in hydrogen for 1 hr. at 600° C. Tensile tests were then made with the following results:

TABLE 1.—*Elongation in 2 Inches*

Treatment	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent.
Miss Leiter's.....	31,500	27.8
Miss Leiter's plus hydrogen anneal at 600° C.	22,800	16.3
Annealed at 725° C. 1 hr. in vacuum.....	32,800	44.0
Annealed at 725° C. in vacuum for 1 hr. plus 1 hr. in H ₂ at 600° C.....	15,200	5.0

These results show that while Miss Leiter's treatment gives copper the properties of which are inferior to those of fully annealed copper, there is a marked improvement in the resistance to gassing.

S. B. LEITER.—The only reason for the copper tube was that any other metal used acted as a reducing agent. Alumina or sand packing caused embrittlement. I think I did use monel metal at one time, and that worked fairly well, but copper seemed to be the safer to use.

In regard to the tensile strength, the work was not conducted with a view necessarily to producing a copper of a greater tensile strength, but a copper that could be used in all cases where reducing action would be likely to occur, or where there would be contact with anything of a reducing nature.

I should not expect the difference in elongation between the specially annealed copper and the 725° C. anneal obtained by Mr. Halliwell, although there might be some slight difference due to difference in grain size produced by the higher temperature. I have not found the anneal at 900° C. in vacuum to produce as tough a copper nor one so resistant to reducing atmospheres as the 900° C. anneal in a neutral atmosphere.

Estimation of Oxygen and Sulfur in Refined Copper

By W. H. BASSETT* AND H. A. BEDWORTH,† WATERBURY, CONN.

(New York Meeting, February, 1926)

THE amount of oxygen present in refined copper bears an important relation to the effects of various impurities on physical properties of copper, as well as the effects of reducing gases at higher temperatures. It seems fitting at this time, when the effects of reducing gases on copper are being discussed, to describe methods that have proved satisfactory for the determination of oxygen and sulfur, and to present some results obtained by investigation of these methods in the authors' laboratory. The procedure for the determination of sulfur is closely interrelated with that for oxygen and has, therefore, been included.

It was first proposed by Hampe¹ that oxides in copper could be accurately determined by the loss in weight sustained by finely divided copper when reduced at red heat in pure hydrogen, or by the weight of water produced. Hampe's method was later modified by Archbutt,² who established the accuracy of the method and demonstrated that equally accurate results were obtained by noting the loss in weight or by weighing the water formed.

The determination of oxygen by heating in carbon monoxide has been proposed by West.³ In our hands this method has given slightly lower results than obtained by heating in hydrogen.

Heath⁴ found that the loss in weight after heating in hydrogen did not represent the true oxygen as cuprous oxide but included also gases derived by the metal from the fuel and refining in the furnace, and any trace of mechanically held moisture. He found, further, that the copper after ignition retained hydrogen equivalent to about 0.01 per cent. Heath proposed to determine the amount of occluded gases by preliminary ignition for 20 min. in pure carbon dioxide—and to correct the error caused by absorbed hydrogen by subsequent ignition and cooling in carbon dioxide, finally replacing this gas with air.

* Technical Superintendent and Metallurgist, American Brass Co.

† Metallurgist, American Brass Co.

¹ *Z. für Berg, Hütten-, und Salinen Wesen in Preussischen Staate* (1873) **21**, 231.

² *The Analyst* (1900) **25**, 253; (1905) **30**, 385.

³ *Jnl. Institute of Metals* (1913) **10**, 371.

⁴ *Jnl. Ind. & Eng. Chem.* (1912) **4**, 402.

Bardwell⁵ has developed a metallographic method for the determination of oxygen along the lines suggested by the work of Hofman, Green, and Yerxa.⁶ This is a very rapid method based on the measurement of the copper-cuprous oxide eutectic areas, and has been found valuable for control work in copper refineries. However, for an exacting analysis, the longer chemical method, weighing the water produced, is to be preferred.

There are, in general, two chemical methods for determining the oxygen in copper. The first, or direct, method is based on collecting and weighing the water produced, and is a rather fussy and tedious procedure but gives accurate and positive results; the second, or indirect, method is based on weighing the residual copper, and is a shorter and more convenient procedure, sufficiently accurate for routine work. Both methods are given in detail at the conclusion of this paper.

APPARATUS

The apparatus consists essentially of a combustion tube, with means for heating it, and a source of hydrogen, with a suitable train for its

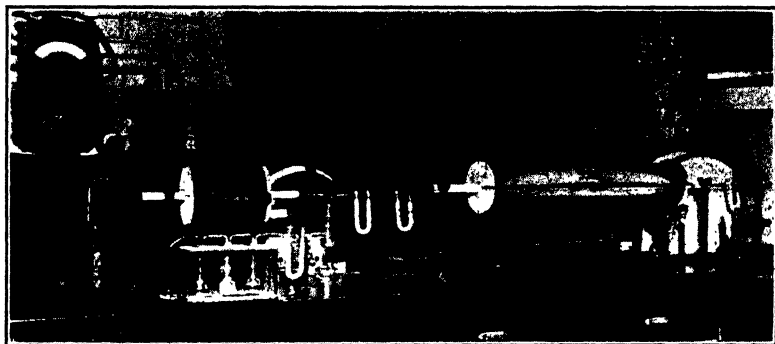


FIG. 1.—HYDROGEN REDUCTION APPARATUS; AMERICAN BRASS CO. LABORATORY.

purification. The hydrogen may be generated in a small Kipp apparatus using pure mossy zinc and 1:1 hydrochloric acid; or it may be obtained in a more convenient form as compressed gas in steel cylinders.

The ignition of the copper may be carried out in a cylindrical silica tube in a combustion furnace of the usual type, heated either electrically or by gas. An apparatus with a furnace of this type is shown in Fig. 1, and diagrammatically in Fig. 6. In a cylindrical tube 5 separate samples may be ignited simultaneously by placing the drillings in porcelain boats,

⁵ *Trans.* (1913) **46**, 742.

⁶ *Trans.* (1904) **34**, 671.

or the tube will hold as much as 200 gm. of copper drillings, which is at times desirable.

In some laboratories, a silica tube, with a bulb at the center holding from 10 to 50 gm. of drillings, is used. This bulb is generally heated by a gas burner. An apparatus with a combustion bulb, as used at the Raritan Copper Works, is shown in Fig. 2. When using this tube for the indirect determination of oxygen, the manipulation is essentially the same except that, instead of weighing the copper alone, the entire tube plus copper is weighed after cooling in hydrogen followed by dry air. For replacing hydrogen by air, a three-way valve is placed ahead of the tube. By weighing the entire bulb plus residual copper, slight amounts of arsenic, antimony, selenium, tellurium, and possibly copper, which are

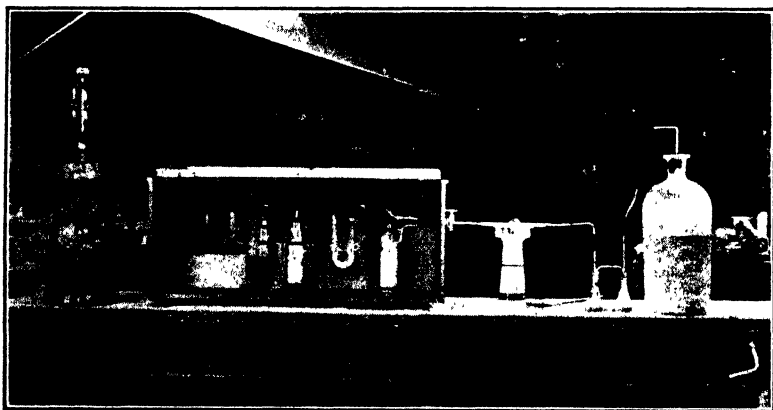


FIG. 2.—HYDROGEN REDUCTION APPARATUS; RARITAN COPPER WORKS LABORATORY.

volatilized and collected as a metallic ring on the tube, are weighed. The weight of these is negligible in the analysis of ordinary refined copper but may be appreciable with more or less impure grades of copper, so that for the analyses of impure coppers, a bulb of this type is advantageous.

The essential requirements of the hydrogen purification train are that it will remove from the hydrogen any oxygen, sulfur, hydrocarbons, acid, and water that may be present. The preliminary furnace (Figs. 1 and 6) containing copper drillings is a feature that has proved very satisfactory for removing oxygen from either hydrogen or carbon dioxide. The renewal of the copper in the preliminary tube is a simple matter and is required but seldom.

The purification of hydrogen may be effected by a train that does not include a preliminary tube of heated copper. A typical example is described below and is shown in Fig. 2. The hydrogen and air trains shown are kept in a box with a glass front and back, which keeps them clean and always ready for use.

1. Bowen large bulb containing 10 per cent. KOH saturated with KMnO_4 , which oxidizes traces of organic matter and neutralizes any free acid that may escape with the gas.

2. Bowen bulb containing concentrated H_2SO_4 .

3. Wash bottle containing a solution of 100 gm. KOH and 7 gm. of pyrogallie acid in 100 c.c. of water, which removes oxygen and carbon dioxide from hydrogen. The hydrogen is then thoroughly dried by passing through

4. Solid KOH.

5. U tube of CaCl_2 .

6. P_2O_5 mixed with glass wool.

This train may be supplemented by (3a) a heated palladium asbestos tube; or as alternatives to (3) and (3a), a tube of stick phosphorus, followed by two tubes of phosphorus pentoxide, may be used.

Carbon dioxide may be generated by the method of Bradley and Hale,⁷ who generate the gas by the action of strong sulfuric acid on a paste of sodium bicarbonate and water; or it may be generated from pure white lump marble or calcite. It may also be conveniently obtained as compressed gas in steel cylinders. The following train may be used for the purification of carbon dioxide gas.

Heated Bowen bulb containing concentrated H_2SO_4 saturated with CrO_3 , for removal of hydrocarbons.

Glass stoppered U tube containing saturated solution of silver sulfate in dilute H_2SO_4 , for removal of sulfides.

Bowen bulb containing concentrated H_2SO_4 .

Heated tube containing copper gauze or drillings, for removal of oxygen.

Glass stoppered U tube containing CaCl_2 .

Glass stoppered U tube containing P_2O_5 opened up with glass wool.

PREPARATION OF SAMPLE

Suitable material for analysis may be obtained by drilling, regulating the size and speed of drill to give fine chips not over 1 mm. thick and free from oxidation. No lubricant is used and, with the proper manipulation in drilling, it is unnecessary to treat the sample subsequently for removal of grease or surface oxidation. Dust and fines should be removed with a screen having 40 meshes to the linear inch, and the drillings should be gone over with a hand magnet to remove particles of iron. Observance of the Copper Specifications of the American Society for Testing Materials⁸ will secure a fair sample of any casting. Turnings, sheet, or wire may be used for this analysis, keeping in mind the limiting thickness of 1 mm.

⁷ *Jnl. Amer. Chem. Soc.* (1908) **30**, 1090.

⁸ A. S. T. M. Standards, 1924. Serial Designation B 34: 20, page 548.

A. M. Smoot⁹ notes that it is almost impossible to remove all the soapy lubricant from some drawn wires by direct washing with alcohol or ether. Such material may be cut in short pieces and digested for a few minutes with a 1 per cent. solution of potassium hydroxide in alcohol, having the liquid warm but not hot enough to oxidize the metal. Finally, wash with water, alcohol and ether, in rapid succession. If a slight abrasion of the skin of the wire is not objectionable, the wire may be scoured with wet sharp silica, which has been ground to pass through a sieve of 40 meshes to the linear inch. The wire may then be cut up, treated with alcohol and ether, and dried off at a low heat.

INVESTIGATION OF METHOD

The characteristics of the reaction of hydrogen with oxygen and sulfur in refined copper from an analytical standpoint have been studied in this laboratory, and the effects of preliminary and subsequent ignition in carbon dioxide have also been determined.

Determination of Oxygen

Table 1 and Fig. 3 show the relative reaction with oxygen at various temperatures. For these tests N. E. C. brand wirebar copper containing 99.952 per cent. copper plus silver and 0.043 per cent. oxygen was used.

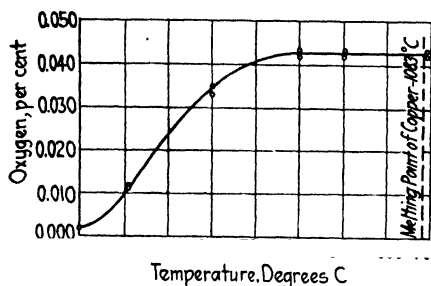


FIG. 3.

FIG. 3.—EFFECT OF TEMPERATURE ON DETERMINATION OF OXYGEN IN COPPER BY HEATING IN HYDROGEN.

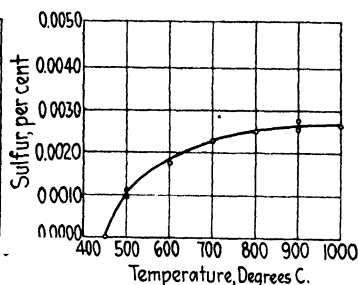


FIG. 4.

FIG. 4.—EFFECT OF TEMPERATURE ON DETERMINATION OF SULFUR IN COPPER BY HEATING IN HYDROGEN.

Drillings not over 0.5 mm. thick were heated in hydrogen at progressively higher temperatures until the copper melted. The temperature was held at each step for 2 hr., and the oxygen was determined by weighing the water produced. The results obtained show that during 2-hr. periods the

⁹ Heath: "Analysis of Copper" (1916) 227.

reaction is appreciable at 400°C. and reaches a maximum at about 800°C., and no further reaction takes place on heating even beyond the melting point of copper.

The question has been raised as to whether the determination by heating copper in hydrogen represents all the oxygen present. It is known that while hydrogen diffuses rapidly through copper at higher temperatures, the steam formed diffuses at a much slower rate, approximately one-fifteenth that of hydrogen.¹⁰ The results of the tests lead us to believe that no appreciable amount of steam remains in the copper after heating drillings in hydrogen at 800° to 850°C. for 3 hr., and that from an analytical standpoint the reaction is complete. The absence of cuprous oxide in samples of copper thus reduced has been confirmed by metallographic examination.

TABLE 1.—*Relation of Determined Oxygen to Temperature of Heating*

Temperature, Degrees C	Oxygen, Per Cent.				
	Test No. 1		Test No. 2		Blank
	Actual	Cumulative	Actual	Cumulative	
300	0.0018	0.0018	0.0018	0.0018	0.0015
410	0.0093	0.0111	0.0096	0.0114	0.0017
600	0.0237	0.0348	0.0215	0.0329	0.0016
800	0.0085	0.0433	0.0090	0.0419	0.0020
900	0.0000	0.0433	0.0000	0.0419	0.0025
1090	0.0000	0.0433	0.0000	0.0419	0.0025

NOTE.—Oxygen as determined by heating at 800°C. for 3 hr. and weighing the copper residue was 0.043 per cent. This is in excellent agreement with the cumulative oxygen shown above, determined by weighing the water produced at different temperatures.

Determination of Sulfur

The characteristics of the sulfur reaction were determined in a similar manner, with the results shown in Table 2 and Fig. 4. Drillings of N. E. C. brand wirebar copper, assaying 99.963 per cent. copper plus silver, were used for these tests. Samples of 100 gm. were heated successively at temperatures up to 1000° C., holding at each for a period of 5 hr. From an analytical standpoint, the reaction begins at about 450° C. and is practically complete after heating at 800° C. to 850° C. for 5 hr.

¹⁰ Norman B. Pilling: Action of Reducing Gases on Hot Solid Copper. *Trans.* (1919) 60, 328.

TABLE 2.—*Relation of Determined Sulfur to Temperature of Heating*

Temperature, Degrees C.	Sulfur, Per Cent.			
	Test No. 1		Test No. 2	
	Actual	Cumulative	Actual	Cumulative
300			0.0000	0.0000
400			0.0000	0.0000
450			0.0000	0.0000
500	0.0010	0.0010	0.0011	0.0011
600	0.0008	0.0018		
700	0.0005	0.0023	0.0012	0.0023
800	0.0002	0.0025		
900	0.0001	0.0026	0.0005	0.0028
1000	0.0001	0.0027		

Preliminary Heating in Carbon Dioxide

Several samples of wirebar copper in the form of drillings were treated with dilute cyanide solution, alcohol, and ether, dried by heating gently, and then given a preliminary ignition in carbon dioxide for 20 min. at 800° C.; the loss in weight is shown in Table 3.

TABLE 3.—*Preliminary Heating in Carbon Dioxide*

Material	Loss in Weight		
	Grams	Per Cent.	Calculated as Hydrogen, Per Cent.
L. N. S. wirebar.....	0.0008	0.008	0.0009
	0.0008	0.008	0.0009
L. N. S. wirebar.....	0.0008	0.008	0.0009
	0.0006	0.006	0.0007
D. R. W. wirebar.	0.0006	0.006	0.0007
	0.0005	0.005	0.0006
	0.0007	0.007	0.0008

According to Heath,¹¹ one-ninth of the original loss obtained in this manner expresses approximately the original gas, as it is principally hydrogen and would abstract oxygen from the copper to form water vapor. As will be observed from the table, the loss calculated as occluded hydrogen is extremely small and, for the purposes of ordinary analysis of refined copper, it is sufficiently accurate to omit this heating in carbon

¹¹ "Analysis of Copper" (1916) 230.

dioxide. In exceptional cases, however, as in the analysis of samples of copper that have been specially treated or prepared, it is necessary to determine occluded gases as loss on ignition in carbon dioxide or by some other means. The subject of occluded gases in refined copper needs further study in order that we may be able to identify positively and estimate such gases as may be present.

Subsequent Heating in Carbon Dioxide

Drillings from several wirebars were ignited and cooled in hydrogen, according to the indirect method for the determination of oxygen, and were then given a subsequent ignition in carbon dioxide for 20 min. at 800° C. The combustion train used for this purpose is shown in Fig. 5. The results obtained are given in Table 4.

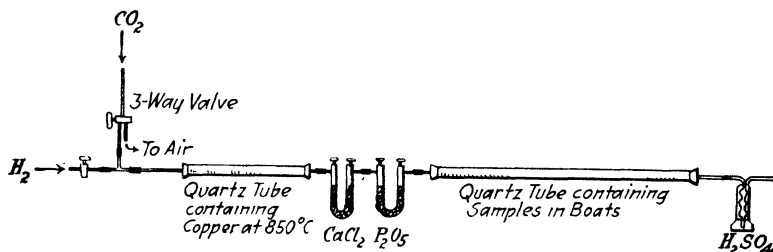


FIG 5.—TRAIN USED FOR IGNITION IN HYDROGEN AND CARBON DIOXIDE.

TABLE 4.—*Subsequent Ignition in Carbon Dioxide*

Material	Weight in Grams		
	After Ignition in Hydrogen	After Subse- quent Igni- tion in Car- bon Dioxide	Change
Special anode, 99.866 per cent. copper + silver.	10.1781	10.1780	-0.0001
	10.0484	10.0485	+0.0001
N. E. C. wirebar, 99.966 per cent. copper + silver.	10.0734	10.0734	0.0000
Tacoma wedge cake, 99.962 per cent. copper + silver.	10.0532	10.0532	0.0000
	10.0413	10.0415	+0.0002
N. E. C. wirebar ^a	10.0262	10.0262	0.0000
	10.0262	10.0262	0.0000

^a After melting and cooling under hydrogen.

These results indicate that, according to the procedure described, subsequent heating in carbon dioxide has no effect and is therefore quite unnecessary.

ACKNOWLEDGMENTS

The authors desire to thank Mr. S. Skowronski, of the Raritan Copper Works, Mr. T. R. Pickard, of the Anaconda Copper Co., Mr. E. Fitzpatrick, of the Nichols Copper Co., and Mr. H. D. Greenwood, of the United States Metals Refining Co., for information, which has been used as a basis for the methods that follow, and for suggestions concerning this work.

DETERMINATION OF OXYGEN

(Direct Method, Weighing H_2O Produced)

Apparatus

The arrangement of the apparatus used is shown in Fig. 6.

A, Hydrogen cylinder containing gas at 1700 lb. per sq. in. pressure.

B, Reducing valve with gages for measuring pressure in tank and in train; the gas is used at 5 to 10 lb. per sq. in. pressure.

C, Valve for regulating flow of hydrogen.

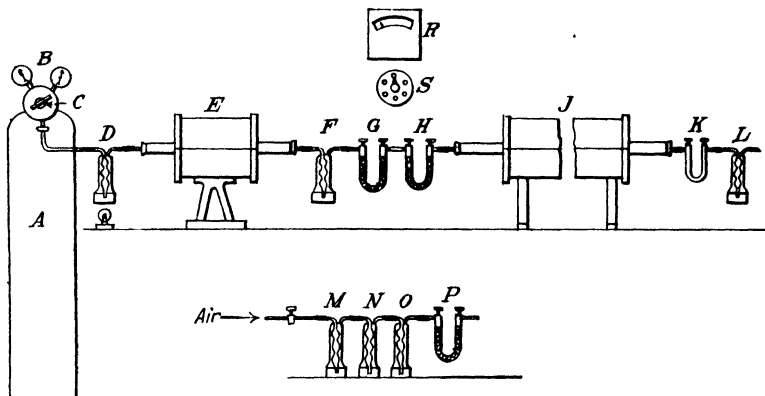


FIG. 6.—APPARATUS FOR DETERMINATION OF OXYGEN IN REFINED COPPER.

D, Bowen bulb containing H_2SO_4 , sp. gr. 1.84, saturated with CrO_3 ; heated by a small electric lamp; used for oxidation of any hydrocarbons present.

E, Electric combustion furnace, hinged type, 8 in. long, with silica tube $\frac{7}{8}$ in. bore by 18 in. long, containing copper drillings previously ignited in hydrogen; for removal of traces of oxygen.

F, Bowen bulb containing H_2SO_4 , sp. gr. 1.84.

G, 6-in. U tube, glass stoppered, containing "Ascarite" (preparation of asbestos impregnated with $NaOH$); for removal of H_2S and any acid. Glass wool is placed in the legs above the reagents and in the stoppers. (All U tubes for this train are filled in a similar manner.)

H, 6-in. U tube, glass stoppered, containing P_2O_5 mixed with dry pumice (6 to 8 mesh) to keep it open; for removal of water.

J, Electric combustion furnace, hinged type, 30 in. long, holding silica tube $\frac{7}{8}$ in. bore by 44 in. long.

K, 4-in. U tube containing P_2O_5 .

L, Bowen bulb containing H_2SO_4 , sp. gr. 1.84.

R, Pyrometer.

S, Multiple switch for operating several furnaces on same pyrometer.

AIR-DRYING TRAIN

M, Bowen bulb containing H_2SO_4 , sp. gr. 1.84.

N, Bowen bulb containing 50 per cent. NaOH.

O, Bowen bulb containing H_2SO_4 , sp. gr. 1.84.

P, 6-in. U tube containing P_2O_5 mixed with pumice.

Method

The copper for use with this method should be in the form of bright, clean drillings or turnings not over 1 mm. thick. Dry in an oven at $105^\circ C$. for 10 min. If the drillings show any sign of surface oxidation or oil, wash with dilute NaCN, rinse three times with distilled water, then twice with grain alcohol, and finally with ether. If the drillings are very oily, wash first with petroleum ether. Dry at $80^\circ C$.

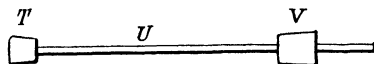


FIG. 7.—APPARATUS FOR PUTTING DRILLINGS IN TUBE.

Weigh out 100 gm. of drillings and place in the tube so that they will be near the middle; the implement shown in Fig. 7 will be useful for this purpose. *T* is a rubber stopper fitting loosely the bore of the tube; *U* is a heavy glass rod 12 to 18 in. long; *V* is a rubber stopper fitting tightly the bore of the tube.

Turn on the hydrogen at the rate of four bubbles per second and start the first furnace *E*, maintaining it at $850^\circ C$. By the time the furnace is up to temperature, the tube will have been swept clear of air. This should be done beforehand to save time. Connect up the main tube containing the sample and continue to pass hydrogen for 30 min. to expel all air. Then place the tube and bulb *K* and *L* in position and start the main furnace *J*. Operate at $850^\circ C$. for 5 hr. Disconnect *K* and *L*, place quickly on the end of the air-drying train and pass a slow stream of air through this for 10 min. The air has been going through the drying train for 30 min. just previous to attaching these.

Remove the tube and bulb from the train and close the stoppers quickly. Disconnect the guard bulb of H_2SO_4 and wipe the P_2O_5 tube

with a warm dry cloth and place it in the balance for 20 min. Just before weighing, open the stoppers for an instant. When the average of the blank tests has been obtained, deduct it from the increase of weight of the tube *K* and calculate the difference to oxygen. Factor H_2O to O is 0.8881.

Continue to run hydrogen through the apparatus until the furnaces have cooled to practically room temperature, then remove sample. The combustion tube, when not in use, should be kept connected with the train and a Bowen bulb containing H_2SO_4 placed at the end of the system.

Notes

1. Glass tubes in the train should be as nearly flush with each other as possible.

2. Rubber connections should be of fresh, thick-wall, pure gum black tubing. Sulfur-free rubber stoppers should be used.

3. Before considering the apparatus fit for making determinations, all the connections and stopcocks of the train must be proved tight by attaching a 6-in. U tube of H_2SO_4 at the end of the combustion tube, subjecting the apparatus to a pressure of gas equal to 2 in. of the acid and noting if any fall of the column takes place in 15 minutes.

4. Before using a new combustion tube for a determination, it should be heated in hydrogen for $\frac{1}{2}$ hour.

5. Before and after making a determination, a blank test should be run in exactly the same manner as the determination. The results of the two blank tests, which should agree and be under 10 mg., are averaged and form a subtractive correction to be applied to the weight of the P_2O_5 tube in the determination.

6. The P_2O_5 tube may be weighed by using another similar P_2O_5 tube as a partial counterpoise.

7. This method gives accurate results but is long and fussy. For this reason, the indirect method of weighing the copper residue is generally used for refined copper, as it is more simple and gives results sufficiently accurate for ordinary requirements. However, in cases where there are larger amounts of arsenic, antimony, selenium, and tellurium present than are usually found in refined copper, it is necessary to use the above method or the combustion bulb.

8. When sufficient arsenic, antimony, selenium, or tellurium is present to interfere by volatilization, the end of the tube is stuffed with glass wool.

9. In order to measure the exact relation between oxygen and copper in a sample, it is necessary to determine the oxygen on the same bottle of clean fresh drillings that is used for the electrolytic assay.

DETERMINATION OF OXYGEN

*(Indirect Method, Weighing Copper Residue)**Apparatus*

The same apparatus is used as in the direct method, except that the tube *K* and bulb *L* are replaced by two Erlenmeyer flasks containing ammoniacal CdCl_2 , as in the determination of sulfur. The air-drying train is not required. Tube *H* and furnace *J* are connected by a piece of rubber tubing sufficiently long to permit transferring the tube to an adjacent cooling rack.

Method

Weigh out approximately 50 gm. of clean bright drillings into five porcelain boats, placing 10.0100 to 10.0200 gm. in each boat. Place the boats in the long tube and, following essentially the same procedure as in the direct method, heat the samples in hydrogen for 3 hr. at 800°C . Remove the Erlenmeyer flasks and determine the sulfur by titration, as hereafter described. Replace the two flasks by a Bowen bulb containing H_2SO_4 and remove the tube from the furnace while still hot and place on a rack alongside the furnace. Allow the tube to cool, using an electric fan as an aid, continuing the flow of hydrogen until cold. Remove the boats from the tube and weigh the copper residue. The loss is considered as oxygen plus sulfur and, having obtained the amount of sulfur, the percentage of oxygen may be calculated.

Notes

1. This method is generally used for the determination of oxygen in refined copper in routine analyses (see note 7 under Direct Method). In addition to oxygen and sulfur, the loss actually includes occluded gases, and slight amounts of arsenic, antimony, selenium, tellurium, and possibly copper. With electrolytically refined copper, however, the error thus introduced is negligible, and the method is sufficiently accurate for ordinary analyses.

2. In special cases, if the presence of occluded gases is suspected, some knowledge of these may be obtained by a preliminary heating in CO_2 at 800° for 20 min., followed by cooling in CO_2 and weighing the residue. The character and behavior of the gases involved should be duly considered in interpreting the loss thus obtained. In the routine analysis of ordinary refined copper, it is sufficiently accurate to omit this ignition in carbon dioxide and ignite in hydrogen directly.

DETERMINATION OF SULFUR

Apparatus

The apparatus required is the same as used for the indirect determination of oxygen.

Solutions Required

Cadmium Chloride Solution.—1 liter contains 40 gm. $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ and 400 cc. NH_4OH , sp. gr. 0.90.

Iodine Solution.—Dissolve 1.2692 gm. iodine with 50 cc. of water and 2.5 gm. NaI . Dilute to 1000 cc. To standardize use arsenious acid solution, which contains 0.001 gm. arsenic per cubic centimeter and is made up by dissolving exactly 0.6600 gm. As_2O_3 in 100 cc. of water containing about 2 gm. KOH , making barely acid with dilute H_2SO_4 and diluting to exactly 500 cc. Place exactly 10 cc. of standard arsenious acid solution in a 300 cc. beaker, dilute to 200 cc. with water, make barely alkaline with NH_4OH , then faintly acid with 1:4 H_2SO_4 with a drop in excess. Add 10 gm. NaHCO_3 , and titrate rapidly with standard iodine solution until the endpoint is reached, employing 3 cc. of starch solution and 3 drops of 10 per cent. NaI solution. Multiply the arsenic value by the factor 0.4277 to obtain the sulfur value. Theoretically 1 cc. of this solution equals 0.00016 gm. sulfur.

Sodium Thiosulfate Solution.—Dissolve 2.482 gm. $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ and 0.1 gm. NaOH in 1 liter of water.

The value of the sodium thiosulfate solution in terms of standard iodine solution should be obtained for every determination. Measure out exactly 10 cc. of iodine solution, and titrate with thiosulfate, having the conditions the same as in the actual determination.

Starch Solution.—Add 6 gm. of soluble starch in suspension with 100 cc. of cold water to 1000 cc. of boiling water. Boil until clear, cool, and add 6 gm. of zinc chloride in 50 cc. of water. (A few drops of HCl may be added to the zinc chloride solution if necessary to clear it.) Mix and preserve in a closely stoppered bottle.

Method

Weigh out 50 to 200 gm. of clean copper drillings and place in the combustion tube. When the sulfur determination is made simultaneously with the oxygen determination the drillings are placed in five porcelain boats, 10.0100 to 10.0200 gm. in each boat. When a larger sample is used, the drillings are loaded directly into the tube, using a clean copper ramrod, taking care not to ram the copper too tightly and that the copper does not extend beyond 3 in. from either end of the furnace.

A glass rod, fitted with rubber stoppers (Fig. 7), may be conveniently used to retain the copper while loading.

In each of two 350 cc. Erlenmeyer flasks place 10 cc. of cadmium chloride solution and 100 cc. of water. Connect the two flasks in series at the end of the furnace, connect up the apparatus and start the hydrogen at the rate of three to four bubbles per second. The heating current is turned on and the apparatus will have been cleared of air by the time the furnace is hot.

The furnace is then operated at a temperature of 850°C. for 3 to 5 hr. Without shutting down, the two absorption flasks are replaced with a single similar flask and the operation continued for 1 hr. longer to determine if the reaction is complete.

To the solution in the flask containing the CdS, an excess of standard iodine solution is added; a little experience will serve as a guide in adding the proper amount. The solution is then acidified with 15 cc. of HCl, sp. gr. 1.19, and cooled in running water; 3 cc. of starch solution are added and the excess iodine is titrated with standard thiosulfate solution.

If the second and third flasks show any CdS, they are treated in a similar manner. This is rarely the case, however, and the clear solution may be used for determining the iodine value of the thiosulfate, by adding 10 cc. of standard iodine solution, 15 cc. of HCl, and titrating as above.

Blank tests may be run in the above manner, and the iodine required, if any, subtracted from the amounts used in the determinations.

Notes

1. This method is a convenient and accurate means of determining sulfur in copper, and with ordinary precautions is not subject to contamination by sulfur-bearing fumes, which are nearly unavoidable in most laboratories, and is consequently much to be preferred to the gravimetric method.

2. The amounts of selenium and tellurium ordinarily found in refined copper do not interfere with this method. With impure coppers carrying larger amounts of selenium, this element will be volatilized to some extent, and a suitable tube filled with glass wool and placed ahead of the cadmium chloride flasks will serve to retain the selenium.

3. In titrating the cadmium sulfide, an excess of iodine is added before acidifying to prevent the loss of any H_2S .

DISCUSSION

G. M. DARBY, Westport, Conn.—What results could be obtained upon brass and bronze in determining oxygen and sulfur by this method?

H. A. BEDWORTH.—Brass and bronze do not lend themselves to ignition in hydrogen. Zinc is driven off and deposits along the tube, and there is a later reaction; that is, a back action, some of your zinc reducing the water vapor evolved, giving zinc oxide. Your results are not dependable; they are erratic and low.

Following a suggestion by T. West in the *Journal* of the Institute of Metals, we tried heating in carbon monoxide, but obtained no better results with that.

G. M. DARBY.—What was the result with sulfur?

H. A. BEDWORTH.—I do not know.

Special Nickel Brasses

BY OLIVER SMALLEY, NEW YORK, N. Y.

(Syracuse Meeting, October,* 1925)

EXCEPT for the work of Guillet, who conducted a systematic investigation on the zinc-replacing value of nickel in brass, and extended his investigation with a view to developing commercial high zinc content nickel brasses, the author does not know of any other systematic research on the subject. The most promising commercial alloys and their physical properties obtained by Guillet are given below:

Copper	Zinc	Nickel	Maximum Stress, Tons Per Sq. In.	Elonga- tion, Per Cent.	Reduction of Area, Per Cent.	Brinell	
55.0	41.0	5.0	24.4	46.5		94	Sand cast.
			22.6	27.0		90	Chill cast.
56.7	39.74	3.35	30.0	43.0	51.7	97	Casting annealed 2 hr. at 750° C.
			33.9	33.0	50.7	144	Cold-drawn bar.
55.15	42.3	2.24	29.8	33.0		116	Casting annealed 2 hr. at 750° C.
			32.3	29.0		151	Cold-drawn bar.

These test results scarcely justify the use of such quantities of so expensive a metal, and could have been obtained from ordinary commercial brass. For purposes of comparison, the physical properties of ordinary brasses, ranging from 70 per cent. to 50.1 per cent. Cu in both the cast and normalized¹ conditions are included in Table 1. These incidentally furnish a useful standard of the properties of castings and of rolled, extruded and forged brass when correctly annealed.

A close study of some of the well-known special brasses containing nickel reveals a series of alloys which bewilder by their complexity, and one can only hazard a guess at the function and commercial value of each of the many elements used.

* Fall Meeting, Institute of Metals Division.

¹ By "normalized condition" is meant the condition that results from mechanical and thermal treatment which completely removes casting structure, internal strain and heterogeneity.

TABLE 1.—*Physical Properties of Pure Brass*

Composition		Condition	Yield Point, Tons per Sq. In.	Maximum Stress, Tons per Sq. In.	Elongation, Per Cent. in 2 In.	Reduction of Area, Per Cent.	Alternating Impact Number	Brinell Hardness Number	Scleroscope Hardness Number
Copper, Per Cent.	Zinc, Per Cent.								
70.0	30.0	As cast.....	6.50	16.70	58.00	57.00	79	55	15
		As forged and annealed.....	8.00	21.50	68.00	65.00	85	57	15
59.0	41.0	As cast.....	8.80	24.90	45.00	49.70	79	90	14
		As forged.....	9.00	26.00	47.00	62.00	87	90	14
		Forged and annealed 650° C. for 1 hr....	7.00	24.00	49.00	55.00		79	12
53.3	46.7	As cast.....	9.00	29.70	24.00	21.50	34	108	18
		As forged.....	9.70	32.80	28.00	30.60	49	114	18
		Forged and annealed 650° C. for 1 hr....	7.50	29.10	22.50	31.60		108	18
51.2	48.8	As cast.....	7.20	26.90	19.00	21.50	27	108	18
		As forged.....	9.20	33.40	37.00	33.50	36	114	18
		Forged and annealed 650° C. for 1 hr....	5.30	29.00	25.00	27.00		108	18
50.19	49.81	As cast.....	6.00	8.80	1.00	1.50	1	108	18
		As forged.....	2.30	15.80	5.00	5.50	9	117	19

For this reason, it is intended in this paper to treat synthetically the development of complex nickel brasses, considering the commoner metals, including nickel, as a third element, proceeding to study nickel as a fourth element on the most promising of the ternary series, as a fifth element on the quaternary series, and so on to the more complex alloys.

SPECIAL BRASSES CONTAINING NICKEL

Name	Cu	Zn	Ni	Al	Mn	Fe	Sn	P	Pb	
Turbadium bronze.....	48.0	46.45	2.0	0.20	1.75	1.00	0.50	0.10		
Turbiston bronze.....	55.0	41.00	2.0	1.00	0.16	0.86		Nil		
German periscope. Maclean Institute of metals, 1921—1.....	53.0	34.00	9.0	0.35	1.50	1.50		Phosphor-tin		
Maclean Institute of Metals, 1921—1.	60.0	34.0	3.0		0.50	2.00	0.25		0.25	Warranted to give 30 tons tensile with appreciable elongation.
Hirst Institute of Metals, 1921—1.....	54.93	38.41	2.59	0.93		1.93	0.19		0.96	
Nickel-manganese bronze.....	53.4	39.0	2.5	0.20	1.70	0.30	2.60		0.30	

To this end, constant conditions were maintained throughout the research, eliminating all variables except the one desired; viz., chemical

TABLE 2

Material	Cu	O ₂	Zn	Ni	Co	Pb	Fe	Al	Si	Sn	Cd	Mn	As
Copper, American electrolytic.....	99 81	0 19		Nil		Nil	Trace						
Zinc.....	Nil		99 99			Trace	Trace		Trace		Trace		
Cupro-nickel.....	92 58			7 25			Trace						
Cupro-cobalt ..	90 00			0 01 9 76			0 20						
Ferro-copper ...	90 00						10 00						
Ferro-zinc. .	0 29		94 10			1 16	4 45						
Aluminum . .	Trace						0 40 99 51	0 09					
Tin.....	Nil		Nil			0 20	Nil	Nil		99 70			0.10
Cupro-manganese. .	72 73					0 09	2 36		0 30				
Phosphorus . . .											0 03	24.35	

composition. For this reason, virgin metal and specially prepared stock alloys of the chemical composition given in Table 2 have been used.

Melting was performed in a 100-lb. pot in a natural-draft coke furnace. The method of introducing the various special metals investigated and the precautions necessary will be detailed under each distinctive heading. To eliminate the variables introduced by sand molds, each melt was poured into a chill iron mold 2½ in. square, the temperature of which was 130° F. The pouring temperature of each alloy was controlled at 10 per cent. superheat.

When it was desired to investigate in the forged or heat-treated conditions, the lower half of the ingot was forged into 1-in. square bars. In the case of cold-working alloys, a 100-lb. ingot was cast 1.05 by 4 in. wide. The lower half was cold rolled in three passes to 0.55 in., annealed at the correct temperature, reduced to 0.45 in. and re-annealed so as to restore to the original cast Brinell hardness number before testing.

Physical Tests

Tensile Tests.—Tensiles were prepared in accordance with the specification of the Engineering Standards Committee, the area being 0.25 sq. in. and gage length 2 in. A permanent set of 0.01 in. is recorded as yield point.

Hardness was determined by the Brinell ball test and the Shore scleroscope; the former being made with a 10-mm. ball under a pressure of 1000 kg. maintained for exactly 30 sec., while the latter test was made with a soft hammer.

Dynamic Stress Tests.—Both alternating and single-blow impact tests were made where possible. In the former, the test piece used was 4 by ½ by ½ in. with a ⅙-in. radius groove milled in the center of one face at right angles to the principal axis. A steel tup having a total weight of 10 lb. was allowed to fall from a height of 18 in. on to the test piece, the first blow being given on the face opposite to the groove, and for every succeeding blow, the test piece rotated through an angle of 180°.

The blows were delivered at a regular rate of 25 per minute, and the number required to break completely the test piece was recorded as the alternating impact number. The single-blow impact test piece was made in the Izod machine, using the standard 10-mm. square test piece, notched 2 mm. deep at an angle of 45° and the striking hammer contacting the test piece at a distance of 22 mm. above the bottom of the notch.

NICKEL BRASS

According to the equilibrium diagram prepared by Guertler and Tammann, nickel alloys with copper in all proportions forming a perfect isomorphous mixture, while the resulting series of alloys, which possess specially useful properties, justify their somewhat high cost. The amount of nickel that zinc will take into solution is so small that it is questionable whether it is soluble at all, although nickel forms a solid solution with up to approximately 50 per cent. zinc.

Functioning as a copper-replacing element, the alloying property of nickel with the ordinary brasses is very similar to that with copper. To introduce pure nickel, a nickel-copper or nickel-zinc stock alloy may be used. Details of composition and test results of the first series of alloys made are given in Table 3.

As Cast

With a constant copper content and reducing the zinc content by the added nickel, 1 per cent. nickel brass shows a slight increase in the yield point, a drop in tensile strength, a decrease in the elongation percentage, but little change in the shock-resisting properties. Exceeding 1 per cent. nickel, there is a general all-round improvement, while the ductility is distinctly superior to that obtained from standard 59:41 brass. Increasing the nickel to 4 per cent. reduces both the strength and the elongation per cent. without affecting the ductility. As the nickel content increases, there is a general decline in the hardness number.

Forged

Nickel acting as a copper-replacing rather than zinc-replacing element, quantities up to 4 per cent. do not materially affect the hot-working properties of ordinary alpha-beta brasses, although alloy N₃ also works admirably cold. The principal features of the test results of alloys N₁, N₂ and N₃ after forging is their general similarity, although the beneficial effect of nickel on the shock-resisting properties is marked.

Microstructure

Under the microscope, nickel is shown to refine not only the crystal grain and reduce the quantity of beta constituent owing to a copper-

TABLE 3.—*Effect of Nickel on Brass*

Series No.	Intended Composition			Actual Composition			Physical Condition	Yield Point, Tons per Square Inch	Maximum Stress, Tons per Square Inch	Elongation, Per Cent in 2 Inches	Reduction of Area, Per Cent	Fracture	Alternating Impact Number	Fracture	Brinell Hardness Number	Scleroscope Hardness Number	Special Comment
	Copper, Per Cent.	Zinc, Per Cent.	Nickel, Per Cent.	Copper, Per Cent.	Zinc, Per Cent.	Nickel, Per Cent.											
N	59.0	41.0	Nil.	58.96	41.04	Nil.	As cast	8.80	24.9	45.0	49.7	Fine, stony, semi-cup and cone	79	Fine, stony, semi-cup and cone	90	14	
							As forged	9.00	26.00	47.5	62.00	Fine, stony, silky, edges	87	Fine, stony, silky, edges	90	14	
N ₁	59.0	40.0	1.0	58.68	40.4	0.92	As cast	9.0	21.1	23.0	36.4	Fine, stony, hackly	77	Fine, stony, hackly	76	13	
							As forged	11.0	26.5	49.0	59.3	Fine, silky, uneven		Fine, silky, uneven			
N ₂	59.0	39.0	2.0	59.0	39.10	1.90	As cast	9.0	23.7	56.0	49.7	Fine, stony, semi-cup and cone	93	Fine, stony, semi-cup and cone	69	11	
							As forged	11.9	26.2	54.0	68.0	Fine, silky, uneven	125	Fine, silky, uneven	90	13	
N ₃	59.0	37.0	4.0	59.02	36.95	4.03	As cast	6.9	18.3	50.0	52.2	Fine, stony, semi-cup and cone	135	Fine, stony, semi-cup and cone	57	9	
							As forged	9.9	25.0	64.0	70.0	Fine, silky, cup and cone	144	Fine, silky, cup and cone	74	10	

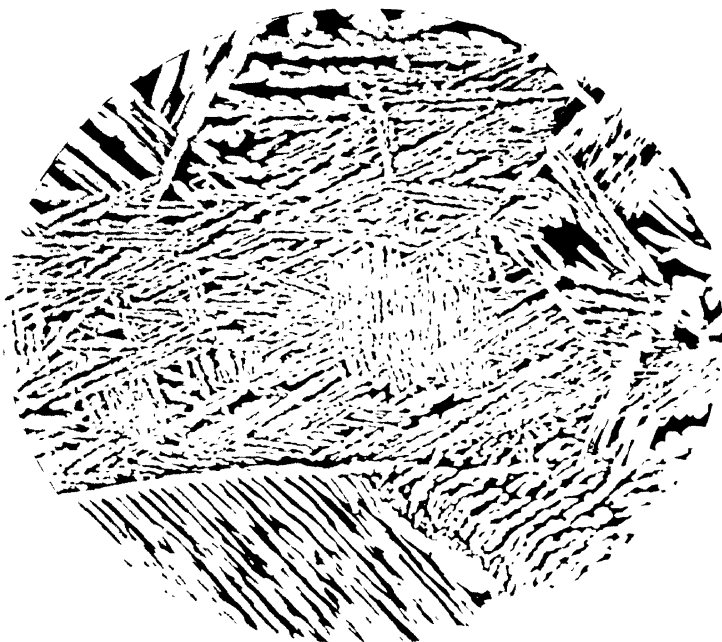


FIG. 1—59 Cu, 41 Zn.



FIG. 2—59 Cu, 40 Zn, 1 Ni.

replacing value of approximately 1.30, but to break down the cell walls of the primary crystal grains; see Figs. 1 to 3, representing the standard 59:41 brass, 59:41 + 1 per cent. nickel and 59:41 + 4 per cent. nickel. These structural changes no doubt explain, together with the increased toughness of the alpha constituent, the improved shock-resisting properties obtained.



FIG. 3—59 Cu, 37 Zn, 4 Ni

ALUMINUM BRASS

As the effect of 1 per cent. aluminum is equal to 5.6 per cent. zinc on both the structure and general physical properties of brass, its influence is directly opposite to that of nickel.

The effect of 1.0 per cent., 1.5 per cent., 2.0 per cent. and 3.0 per cent. aluminum on the mechanical properties of 59:41 brass in both the cast and forged conditions are embodied in Table 4.

Castings

Prominence is given to the remarkable effect of small quantities of aluminum in increasing the yield point and strength, which is accompanied by a corresponding fall in ductility and shock-resisting properties. The rapid strengthening limit of aluminum seems to be 1.35 per cent., although maximum strength is not reached until 3 per cent. has been added. Exceeding 3 per cent., the strength falls away and on the visible inception of the gamma constituent, the alloy loses its ductility.

TABLE 4.—*Effect of Aluminum*

Series No.	Intended Composition		Actual Composition					Physical Condition	Yield Point, Tons Per Square Inch	Maximum Stress, Tons per Square Inch	Elongation, Per Cent in 2 inches	Reduction of Area, Per Cent.	Fracture	Alternating Impact Number	Fracture	Lead Impact Number	Brinell Hardness Number	Scleroscope Hardness Number
	Copper, Per Cent.	Zinc, Per Cent.	Aluminum, Per Cent.	Iron, Per Cent.	Lead Per Cent													
A	59.0	41.0	Nil.	58.96	41.04	Nil	As cast	8.80	24.90	45.0	49.7	Fine, stony, semi-cup and cone edges	79	Fine, granular, silky edges	90	14		
							As forged	9.00	26.00	47.5	62.0	Fine, stony, silky edges	87	Fine, granular, silky edges	90	14		
A ₁	59.0	40.0	1.0	59.48	39.52	1.00	As cast	14.8	32.0	30.0	33.5	Coarse, stony and acicular. Trace of intercrystallinity along 2 in parallel	46	Fine, stony, vitreous	114	21		
							As forged	11.1	31.3	41.0	44.6	Fine, stony. Free from intercrystallinity	67	Fine, stony, semi-morphous	104	18		
A ₂	59.0	39.5	1.5	58.35	40.11	1.54	As cast	16.4	35.2	17.0	18.5	Between 12 and 14	23	Coarse, crystalline, stony	129	21		
							As cast	16.0	36.4	16.0	21.5	As A ⁴ except it is not so strongly crystalline or so highly colored	25	Coarse, crystalline, stony	138	22		
A ₃	59.0	39.0	2.0	58.26	38.56	2.18	As forged	11.7	37.4	27.0	33.5	Similar to A ⁴ but more crystalline	39	Coarsely crystalline strongly laminated	143	23		
							As cast	22.3	42.0	18.5	21.5	Coarse; crystalline	27	Fine, stony, inclined to exhibit inter-crystallinity	159	25		
A ₄	59.0	38.0	3.0	59.85	37.13	3.02	As forged	19.0	40.3	24.5	30.6	Brilliant red luster. Highly crystalline. Brilliant red luster. Slight intercrystallinity along 2 in. parallel	41		154	23		

Forged Condition

The ordinary alpha-beta aluminum brasses do not present any difficulty in working and may be readily forged, rolled or extruded. Their increased hardness, however, demands a relatively greater blow or pressure; and readily hardening up, cannot be worked down to small sections with the ease of Muntz metal. All beta aluminum brasses suffer from a long period of heat fragility, regardless of their chemical composition. There is, however, no difficulty in working hot, although the range of temperature permissible is limited. Ordinary beta brasses of the copper-zinc series have a period of heat fragility extending from 315° to 455° C.; beta brasses of the copper-zinc-aluminum series, approximately from 226° to 558° C.

In the beta alloys under consideration forging was performed between 700° and 620° C. They may be worked at temperatures above 700° C., but there is great danger in doing so owing to the abnormally rapid crystal growth at such temperatures, which is not readily eliminated by a continuance of the work at lower temperatures as obtains in alloys having a duplex structure. At the best, high-tenacity beta brasses are brittle alloys, and slight overheating renders them unsafe in service.

The effect of forging is shown to have reduced the yield point, to have affected the strength and hardness very little, and to have improved both the ductility and shock-resisting powers.

Microstructure

Figs. 4 and 5 show the effect of substituting 1.0 per cent. and 1.5 per cent. aluminum for the same amount of zinc in a 59 per cent. copper brass. They amply demonstrate the coefficient of equivalence referred to and explain the hardening propensities of aluminum.

TIN BRASS

In complex high-strength brasses where ductility is of importance, 0.75 per cent. is the maximum quantity of tin that may be used. In naval brass, 1.0 per cent. tin seems to be the useful limit. The constitution of this series has been closely studied by Hudson, Carpenter, Hoyt, Turner, and others.

The standard 59:41 brass will take into solution approximately 1.0 per cent. tin when sand cast and 1.2 per cent. when chill cast. With an increasing zinc content, the figure is increased to a maximum of 1.8 per cent. at 47 per cent. zinc. In this paper, it is proposed to consider 0.50 per cent., 1.0 per cent., 2.0 per cent. and 3.0 per cent. tin brasses with 59 per cent. copper base. Conditions of manufacture were those

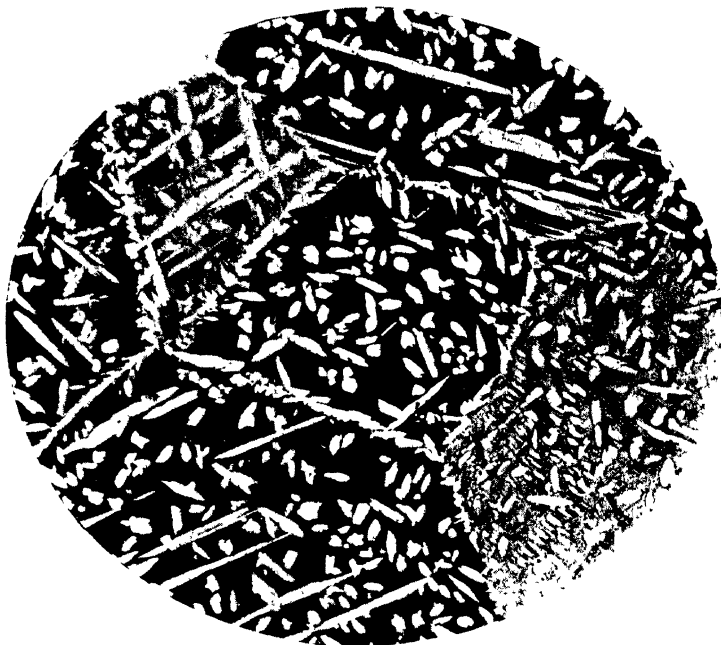


FIG. 4—59 Cu, 40 Zn, 1 Al

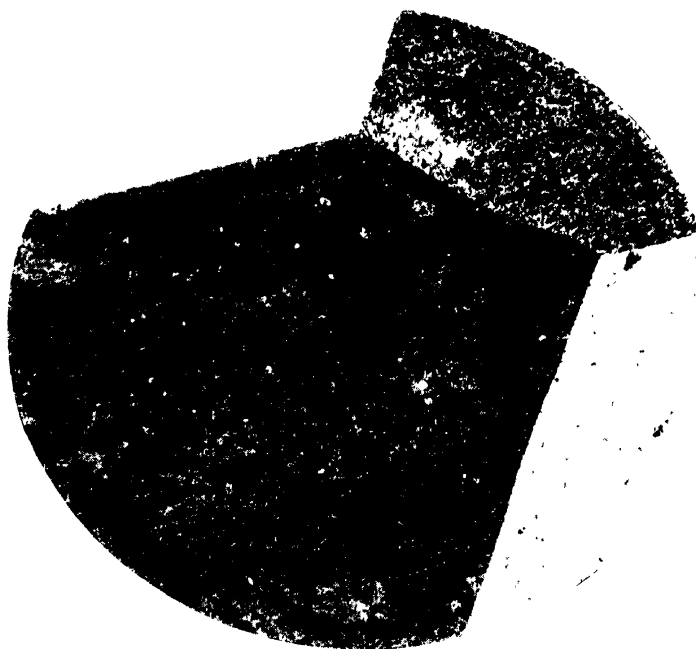


FIG. 5—59 Cu, 39.5 Zn, 1.5 Al.

TABLE 5.—*Effect of Tin on Brass*

Series No	Intended Composition			Actual Composition					Physical Condition	Mechanical Properties				Fracture	Alternating Impact Number	Fracture	Brinell Hardness Number	Scleroscope Hardness Number
	Copper, Per cent	Zinc, Per Cent	Tin, Per Cent	Copper, Per Cent	Zinc, Per Cent	Tin, Per Cent	Iron, Per Cent	Yield Point, Tons per Square Inch		Maximum Stress, Tons per Square Inch	Elongation Per Cent in 2 Inches	Reduction of Area, Per Cent						
S	59 0 41 0	Nil	Nil	58 96 41 04	Nil	Nil	As cast	8 80 24 90	45 0 49 70	Fine, stony, semi-cup and cone	79	Fine, granular, silky edges	90	14				
							As forged	9 00 26 00	47 5 62 00	Fine, stony, silky edges	87	Fine, granular, silky edges	90	14				
S ₁	59 0 40 5	0 5	59 95 39 38	0 47	0 20	As cast	11 0 26 2	44 0 42 0	Fine, stony, silky edges More or less hackly	77	Fine, silky, semi-vitreous	87	13					
						As forged	15 6 28 8	38 0 60 0	Fine, granular, silky edges Cup and cone	113	Fine, granular, semi-vitreous in upper half	107	15					
S ₂	59 0 40 0	1 0	58 90 40 10	1 00	Trace	As cast	9 6 26 7	32 0 33 5	Fine, stony, silky edges Trace crystallinity existing as exhibited by S ₃	47	Fine, crystalline with a slight appearance of laminated crystals exhibited by S ₃	98	15					
						As forged	13 6 28 6	38 0 44 6	Fine, granular, silky edges Semi-cup and cone	107	Fine, granular, semi-vitreous in upper half	107	16					
S ₃	59 0 39 0	2 0	58 82 38 76	2 11	0 31	As cast	11 8 26 1	13 0 15 0	Short, coarsely crystalline consisting of grayish, stony crystals existing alternately	5	Short, grossly coarse laminated crystals	114	20					
S ₄	59 0 38 0	3 0	59 17 37 63	2 98	0 22	As cast	16 4 21 25	1 5 3 2	Coarse, gray and stony colored Highly crystalline	1	Short, coarse, laminated crystals	136	23					

outlined for the nickel and aluminum brasses, introducing the zinc and the tin, as such, last. Physical test results are given in Table 5.

As Cast

One-half per cent. tin increases the yield point and maximum stress 2.25 and 1.3 tons respectively without affecting the elongation, reduction of area and alternating-impact strength. Increasing to 1.0 per cent. hardens without strengthening and impairs both ductility and impact strength. This embrittlement is accentuated by additional quantities of tin, as shown by alloys S₃ and S₄, the latter having little strength and no ductility.

Forging

No difficulties were encountered in the forging of alloys S₁ and S₂, which worked with the ease of Muntz metal. The test results of alloys S₃ and S₄ in the "cast" condition did not justify consideration in the forged condition and no improvement could be obtained by special heat treatment. After forging, the yield point of alloy S₁ is raised 6.6 tons per sq. in. and the maximum stress, 2.8 tons per sq. in., but the elongation per cent. is slightly reduced. The drop in ductility, however, is not of real importance, the alternating impact figure being increased no less than 15 per cent. While the physical properties of the 1 per cent. tin brass in the cast state are inferior to those of 59:41, they are superior after forging, but it is clearly demonstrated that 1 per cent. is the limit of practical utility.

Structure

There is little perceptible difference in the structure of an alpha-beta brass containing 0.5 per cent. tin and that containing 1.00 per cent. Exceeding 1 per cent., a brittle copper-tin compound makes its appearance. The effect of this constituent is shown to be similar to the "gamma" compound in ordinary brass.

These results show clearly that tin cannot be regarded in the same light as either nickel or aluminum, as it is neither a copper- nor a zinc-replacing element, although, structurally, attempts have been made to consider it a zinc-replacing element, giving to it a coefficient of equivalence of 2.

IRON BRASS

Copper and iron form a heterogeneous series of alloys except at the terminals of the curves. Between these proportions the alloys consist of two constituents; the one rich in iron, the other rich in copper. Carbon and copper do not associate in any form and the presence of carbon in

iron reduces the solubility to an extent that neither steel nor cast iron can be satisfactorily alloyed with copper, but merely exist side by side as a mechanical mixture. Zinc readily unites with iron.

The effect of iron on ordinary brass has been studied by F. Johnson, Comstock, Guillet, and Millington and the available data place our knowledge of iron brasses on a secure foundation.

In this series the iron was introduced by means of a 10 per cent. iron, copper-iron alloy which was melted alongside with copper except in the case of alloy 1F₂, when the iron was introduced by means of a zinc-iron stock alloy. Other conditions of manufacture were those adopted throughout the series. No peculiarities or difficulties were encountered either in melting or in pouring.

As Cast

The effect of 1.0 per cent., 1.5 per cent., and 2.5 per cent. iron on the tensile, hardness and impact strength of an alpha-beta brass of 59 per cent. copper content is shown in Table 6. In castings, 1.0 per cent. iron improves both the tensile and shock-resisting properties. No improvement of strength is to be gained by exceeding this quantity, while the shock-resisting properties tend to fall; particularly is this true in the case of alloy 1F₂. The low ductility of this alloy, however, is accounted for to some extent by the crystalline form of the impurities introduced by the zinc-iron stock alloy used, and is typical of the every-day troubles encountered when the impure stock alloy is used for the purpose of introducing iron.

Forged Condition

Hot working results in an all-round improvement of the tenacity of each alloy, having little influence on the ductility, except in the case of alloy 1F₂, which improvement is as expected.

Microstructure

The outstanding feature is the refining effect of small quantities of iron on the texture. The author's explanation is that each of the finely divided particles of the high melting point iron-rich particles distributed throughout the molten metal acts or tends to act as a nucleus for the germination of a primary crystal grain. The solubility content of these particles is not known, but they are discernible under the microscope only at high magnifications, when the quantity exceeds 0.35 per cent.; at 1.0 per cent. they are clearly visible at ordinary magnifications; above 1.0 per cent. they begin to aggregate and become visible to the eye from a polished surface.

TABLE 6.—*Effect of Iron on 59:41 Brass*

Series No.	Composition			Physical Condition	Yield Point, Tons per Square Inch	Maximum Stress, Tons per Square Inch	Elongation, Per Cent. in 2 Inches	Reduction of Area, Per Cent.	Fracture	Alternating Impact Number	Fracture	Brinell Hardness Number	Scleroscope Hardness Number
	Copper, Per Cent.	Zinc, Per Cent.	Iron, Per Cent.	Lead, Per Cent.									
1F	58.96	41.04			As cast	8.80	24.90	45.00	Fine, stony, semi-cup and cone	79	Fine, granular, silky edges	90	14
					As forged	9.00	26.00	47.50	Fine, stony, silky edges	87	Fine, granular, silky edges	90	14
1F ₁	59.37	39.68	0.95	Nil	As cast	9.40	26.80	44.00	Fine, silky semi-cup and cone	95	Fine, silky vitreous	90	13
					As forged	13.90	28.80	44.00	Fine granular cup and cone. Silky edges	81	Fine, stony semi-vitreous	107	14
1F ₂	59.04	38.95	1.56	0.45	As cast	11.00	26.80	33.00	Fine, stony granular semi-cup and cone	31	Fine, stony	85	13
					As forged	13.60	27.60	43.00	Fine granular cup and cone, silky edges	49	Fine, stony, inclined to be vitreous	98	15
1F ₃	59.12	38.36	2.52	Nil	As cast	10.00	26.50	46.00	Fine, silky, semi-cup and cone	71	Fine, slightly more silky in appearance than F ₁ .	92	14
					As forged	15.80	28.30	39.00	Stony, granular, uneven	79	Fine, stony, semi-vitreous	110	16

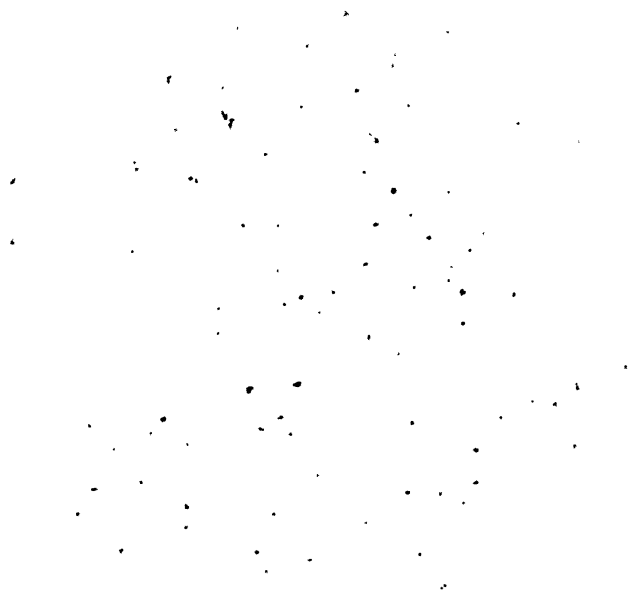


FIG. 6—59 Cu, 40 Zn, 10 Fe

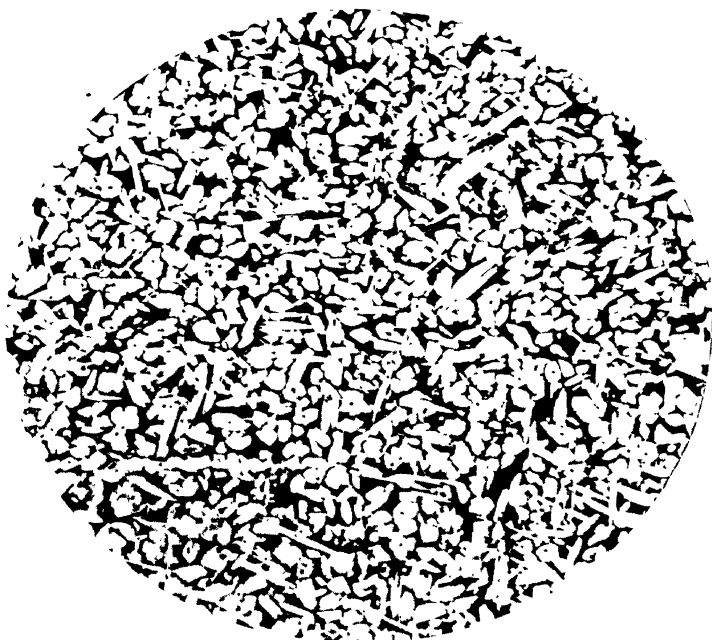


FIG. 7.—59 Cu, 40 Zn, 10 Fe.



FIG. 8—59 Cu, 39.5 Zn, 1.5 Fe.



FIG. 9.—59 Cu, 38.5 Zn, 2.50 Fe.

Fig. 6 shows the form and quantity of the iron compound present in alloy 1F₁. Fig. 7 shows the refining effect of this iron compound on the microstructure. Fig. 8, representing alloy 1F² as cast, etched shows that there is no further refining of the grain on increasing the iron content. Figs. 9 and 10 represent alloy 1F₃ containing 2.52 per cent. iron, unetched and etched respectively. Except for the presence of larger quantities of the iron-rich compound, no other structural changes are apparent. Guillet regards iron as a zinc-replacing element, 0.90 per cent. iron being equal to 1.0 per cent. zinc. This, however, is erroneous; nor does it function in the same way as any of the other elements previously considered.

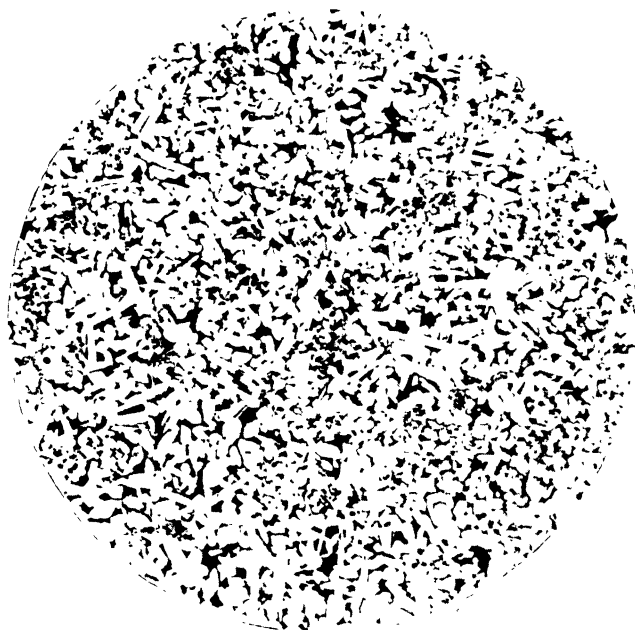


FIG 10—59 Cu, 38.5 Zn, 2.50 Fe.

EFFECT OF IRON ON 53.3:46.7 BRASS

In view of the fact that the hardness of pure iron is similar to that of 59:41 brass, its limitations as a hardener or a strengthener will be to ordinary brass containing up to 41 per cent. zinc. On the assumption that it is neither a copper- nor a zinc-replacing material, but exerts merely a mechanical effect on the mode of the crystal growth, its common use in high-tenacity brasses, therefore, must be that of a grain refiner or densener. To investigate this, three alloys were made, designated 2F, 2F₁ and 2F₂. The first contained 53.3 per cent. copper and 46.7 per cent. zinc; the second, 51.5 per cent. copper, 47.5 per cent. zinc and 1 per cent. iron; while the last one was made up of 51.0 per cent. copper, 47 per cent. zinc and 2 per cent. iron. The copper and zinc were adjusted

so as to bring each to a similar position in the beta phase area of the copper-zinc constitutional diagram, assuming the iron, of course, to be without influence.

Mechanical Properties

The chemical composition and physical test results obtained are given in Table 7. These indicate iron to be detrimental to the ductility in the cast state, but beneficial when forged. It will be observed also, that forging lowers the yield point of alloy 2F but raises the maximum stress; that it increases both the yield point and maximum stress of alloy 2F₁, and lowers both the yield point and maximum stress of alloy 2F₂, though each was treated similarly and had the same Brinell hardness in both the cast and the forged conditions.

Microstructure

The mechanical properties of beta brass being unaffected by normal heat treatment—both tenacity and ductility being similar, no matter what the rate of cooling—the changes responsible for the peculiar test results, which are typical of those obtained from complex beta brasses, must be attributable to one or all of the following causes:

1. Internal molecular changes or structural inversion of the beta constituent.
2. Geometrical outline of the crystal grains.
3. Mode of distribution of the iron-rich constituent.

Actual examination proved that iron renders both the internal and external form of the crystal grain more regular and that this is the principal cause of its embrittling properties in cast brass. Forging, refining and effecting an interpenetration of adjacent crystal grains explains the improved ductility wrought by mechanical work.

The effect of the iron-rich particles is unimportant, providing they are uniformly distributed and are in a fine state of division.

Having established the functions of the third element, the effect of nickel on the more complex alloys may now be studied.

NICKEL-ALUMINUM BRASSES

Manufacture

Constant conditions were maintained throughout and were those adopted in the ternary series. The nickel was introduced by means of the standard copper-nickel stock alloy although it may be introduced as an alloy of aluminum and nickel, or of copper and nickel, or in the form of shot nickel.

Nickel is not detrimental to the casting qualities of this series of brasses, and nickel-aluminum brasses do not call for the care necessary

TABLE 7.—*Effect of Iron on 53:47 Brass*

Mark	Actual Composition				Physical Condition	Yield Point, Tons per Square Inch	Maximum Stress, Tons per Square Inch	Elongation, Per Cent in 2 Inches	Reduction of Area, Per Cent.	Fracture	Alternating Impact Number	Brinell Hardness Number	Scleroscope Hardness Number	Number of Crystal Grains per Square Centimeter
	Copper, Per Cent.	Zinc, Per Cent.	Iron, Per Cent.	Lead, Per Cent.										
2F	53.41	46.59	Nil.	Nil.	As cast	9 00	29 70	24 00	21 50	Coarse, crystalline, exhibiting brilliant luster	34	114	15	39
					As forged	8 70	32 80	28 00	30 60	Coarse flaky, exhibiting brilliant yellow crystalline facets, extension uniform over the 2 in. parallel	49	114	15	488
2F ₁	51.72	47.23	1.05	Nil.	As cast	8 00	30 90	16.00	15 00	Fine, crystalline, exhibiting brilliant crystal facets	9	114	15	1765
					As forged	9 60	33 00	38 00	33 50	Flaky, uneven	39	114	15	2336
2F ₂	50.77	47.03	2.20	Nil.	As cast	11 10	33 00	17.00	15 00	Fine, crystalline exhibiting brilliant crystal facets	9	114	17	2314
					As forged	8 60	30 60	43 00	44.60	Fine, yellow, almost granular	85	121	17	2200

with manganese-aluminum brasses to avoid overlaps and surface unevennesses, brought about by rapid oxidation in the molten state.

1.5 Per Cent. Aluminum-Nickel Brasses

Physical Tests.—The effect of 3.0 per cent. nickel on a 1.5 per cent. aluminum 59 per cent. copper brass, and on a 1.5 per cent. aluminum 56 per cent. copper brass is shown by alloys AN₃ and AN₆ respectively, Table 8. The substitution of 3.0 per cent. zinc by 3.0 per cent. nickel (alloy AN₃) resulted in an all-round improvement of the physical properties, although the strength and hardness are slightly reduced. The increased ductility and shock-resisting properties, however, more than compensate for the lowered strength.

By reducing the copper content to 56 per cent. (alloy AN₆) the strength and hardness are improved, but the ductility and impact strength are reduced, so that equal physical properties may be obtained from ordinary aluminum beta brass.

Structure.—While alloy 13 consists wholly of the beta constituent, alloy AN₃ is an alpha-beta brass of approximately 45 per cent. alpha constituent and 55 per cent. beta. Unetched, this alloy exhibits the presence of a blue compound which is distributed uniformly in a finely divided state throughout the mass. Alloy AN₆ exhibits features similar to those of alloy AN₃, except that the beta constituent now predominates—approximately 80 per cent. to 85 per cent.—with the result that the hard beta crystal grains are surrounded by a thin envelope of the alpha constituent, which structural disposition explains the poor ductility and impact strength obtained.

3.0 Per Cent. Aluminum-Nickel Brass

As Cast.—Increasing the copper content to 60 per cent. and the aluminum to 3.0 per cent., the effect of nickel is to reduce the yield point and strength without influencing the ductility or impact strength—alloy AN₁, Table 9.

As Forged.—When forged this difference is reversed and alloy AN₁ gives a higher yield point, ductility and impact strength.

Structure.—In themselves, these test results suggest nickel to be of little actual value and, because of the cost, judgment is against its use. For ordinary foundry practice, this is a sound decision, for if nickel be introduced into aluminum brasses without a knowledge of the structural changes brought about when aluminum and nickel are used conjointly, the results will be very disappointing. This is emphasized by the fact that we do not possess any information on the structural changes brought about by aluminum and nickel in combination. We know that 1.0 per cent. aluminum is equal to 5.6 per cent. zinc and that 1.0 per cent. nickel is equal to 1.3 per cent copper, but the replacing value of zinc and

TABLE 8.—*Effect of Nickel on 1.5 Per Cent. Aluminum Brass*

Series No.	Intended Composition					Actual Composition					Physical Condition	Yield Point, Tons per Square Inch	Maximum Stress, Tons per Square Inch	Elongation, Per Cent. in 2 Inches	Reduction of Area, Per Cent.	Fracture	Impact Number	Fracture	Brinell Hardness	Scleroscope	Crystal Grains per Square Centimeter	
	Copper, Per Cent.	Zinc, Per Cent.	Aluminum, Per Cent.	Nickel, Per Cent.	Iron, Per Cent.	Copper, Per Cent.	Zinc, Per Cent.	Aluminum, Per Cent.	Nickel, Per Cent.	Iron, Per Cent.												
13	59 00	39 50	1 50	Nl.		58 35	40 11	1 54	Nl.		As cast	16 4	35 2	17 0	18 5	Coarse, crystalline, stony	23	Coarse, crystalline, stony	129	21		
AN ₂	59 00	36 50	1 50	3 00	0 10	58 88	36 51	1 43	3 08	0 10	As cast	11 00	30 80	34 00	33 50	Even, oblique, silky	55	Fine, granular, traces of crystallinity, silky edges	101	15		174
											As forged	21 20	34 70	28 00	33 50	Even, oblique, silky	41	Fine, silky, inclined to be fibrous (lamellations)	148	27	Could not be counted	
AN ₆	56 00	39 50	1 50	3 00		55 60	39 38	1 64	3 27	0 11	As cast	14 00	34 70	15 00	18 30	Fine, stony, short, indications of crystallinity	17	Stony, mixed granular and crystalline	117	25		
											As forged	15 20	37 70	22 50	23 00	Fine, stony, granular, even short	43	Short, granular	129	28		

TABLE 9.—*Effect of Nickel on 3 Per Cent. Aluminum Brass*

Series No.	Intended Composition						Actual Composition						Physical Condition	Yield Point, Tons per Square Inch	Maximum Stress, Tons per Square Inch	Elongation, Per Cent in 2 Inches	Reduction of Area, Per Cent.	Fracture	Impact Number	Fracture	Brinell Hardness, Number	Scleroscope Hardness Number	Crystal Grains Per Square Centimeter
	Copper, Per Cent.	Zinc, Per Cent.	Aluminum, Per Cent.	Nickel, Per Cent.	Iron, Per Cent.		Copper, Per Cent.	Zinc, Per Cent.	Aluminum, Per Cent.	Nickel, Per Cent.	Iron, Per Cent.												
15	59 00	38 00	3 0	Ni.			59 85	37 13	3 02	Nil			As cast	22 3	42 0	18 5	21 5	Coarse, crystalline, brilliant red luster	27	Coarse, crystalline	159	25	
													As forged	19 0	40 3	24 5	30 6	Coarse, crystalline, brilliant red luster	41	Fine, stony, inclining to exhibit intercrystallinity	154	23	
ANi	60 00	34 00	3 00	3 00			60 50	33 65	2 89	2 96			As cast	16 60	36 70	19 00	21 50	Fine, stony, semi-cup and cone	27	Fine, stony, short	125	18	284
													As forged	21 00	39 80	28 00	33 50	Free from intercrystallinity fine, granular, silky, edges uneven	46	Fine, stony, slight silky tinge	148	27	318
													Forged, reheated and quenched in water from 780° C and reheated to 450° C.	28 40	46 20	18 00	21 50	Fine, earthy, semi-cup and cone			272	32	318

copper cannot be so simply calculated owing to the formation of the rich aluminum-nickel alloy, to which reference has already been made.

The effect of the nickel in alloy AN₁ has been to restore the alpha constituent, the all-beta structure of alloy 15 being replaced by one containing only 60 per cent. of the beta constituent. For this reason, alloy AN₁ belongs to a different series from alloy 15 and the two are not comparable.

The real value of AN₁ lies in the fact that it is an alpha-beta brass of promising unique physical properties. It is free from the period of low temperature brittleness, common to most high-strength brasses, and is highly resistant to corrosion. It possesses the mechanical properties of the more expensive monel metal, but is simpler to manufacture. It retains a good strength and ductility at temperatures up to 500° C. It may be worked hot or cold. It is a safe alloy to forge, stamp or extrude, and does not require the rigid control necessary to high-tensile beta brasses, nor is it so readily ruined by slight overheating. It is peculiarly susceptible to the influence of heat treatment, however, and yields a Brinell hardness range from 110 to 285. After suitably hardening by water-quenching from 780° C. and tempering by reheating to 450° C. for 30 minutes, cooling off in the furnace, this alloy gave the improved physical tests shown, which compare favorably with some of the best made forged and heat-treated carbon steels, while it is free from grain weakness.

Thus it will be seen that this alloy has a field pregnant with possibilities for the manufacture of high-strength castings which have to withstand corrosion, service conditions at high temperatures and superheated steam at high pressures.

4 Per Cent. Aluminum-Nickel Brass

As Cast.—Reducing the copper content 1 per cent. and increasing the aluminum 1.0 per cent. alloy AN₂, Table 12, shows that the effect of 3.0 per cent. nickel is to yield an alloy of exceptionally high strength, elasticity and wearing properties but of low ductility and impact strength, although it exhibits a remarkably fine and close grain.

As Forged.—After forging, the yield point and maximum strength are further increased without any material change in ductility or impact strength.

Structure.—Structurally it is an all-beta brass and is comparable with alloy 15. The principal feature of the nickel is its efficacy as a grain refiner, apparently due to the germ effect of the high-melting-point aluminum-nickel particles disseminated throughout the molten metal, *i. e.*, it behaves much in the same way as iron in ordinary brass.

5 Per Cent. Aluminum-Nickel Brass

To come into line with alloy AN₁, *i. e.*, to produce an alpha-beta brass containing 5 per cent. aluminum, it was necessary to increase the copper content to 70 per cent.

As Cast.—The test results obtained from both the aluminum and the aluminum nickel brass of such a composition are given in Table 10. These show that in reproducing the ordinary muntz-metal structure from a 70 per cent. copper brass by the aid of aluminum, the results are negative, for while the yield point and strength are good, the ductility and impact strength are poor. By further reducing the zinc content by 3.77 per cent. of nickel, the effect has been to further increase the strength and restore the ductility and impact strength.

As Forged.—In the forged condition both alloys are worthy of consideration where special strength and ductility are required. Economically, however, these properties are not improved commensurately with their increased cost, which reduces their practical utility.

Structurally, they display the features of the aluminum-nickel brasses previously considered, except for greater quantities of the aluminum-nickel particles of larger dimension.

IRON-ALUMINUM BRASS

Before proceeding to study the effect of nickel-iron-aluminum brasses, it is necessary to consider briefly the effect of iron on aluminum brass. For this purpose, aluminum brass, mark No. 6—copper 59 per cent., zinc 38 per cent., aluminum 3 per cent.—will be used. Four casts were made, designated No 6, AF₃, AF₂, and AF₁, of similar chemical composition, with the exception of the iron content which was nil, 0.50 per cent., 1.0 per cent. and 2.0 per cent. respectively. The physical tests obtained are given in Table 11. The actual compositions are slightly different from those intended, AF₃ contained 0.61 per cent. iron instead of 0.50 per cent. and AF₁ 1.87 per cent. iron instead of 2.0 per cent. The other elements analyzed are as intended.

Alloy AF₃

As Cast.—The effect of 0.61 per cent. iron is to increase slightly both the tenacity and hardness, although this is unappreciable.

As Forged.—Forging resulted in a distinct drop of both the yield point and the tenacity, but improved the ductility. Considered broadly, the effect of this quantity of iron has been very slight.

Alloy AF₂

As Cast.—One per cent. iron effected an all-round improvement. Castings from this alloy compare favorably with forgings made from alloy 6.

TABLE 10.—*Effect of Nickel on 5 Per Cent. Aluminum Brass*

Series No.	Intended Composition					Actual Composition					Physical Condition	Yield Point, Tons per Square Inch	Maximum Stress, Tons per Square Inch	Elongation, Per Cent in 2 Inches	Reduction of Area, Per Cent	Fracture	Impact Number	Fracture	Brinell Hardness Number	Stereoscope Number	
	Copper, Per Cent.	Zinc, Per Cent.	Aluminum, Per Cent.	Nickel, Per Cent.	Nickel, Per Cent.	Copper, Per Cent.	Zinc, Per Cent.	Aluminum, Per Cent.	Nickel, Per Cent.	Iron, Per Cent.											
10	70.00	25.5	4.5	Nil.	Nil.	69.13	26.32	4.55	Nil.	Trace	As cast	17.6	31.9	8.0	11.7	Coarse, crystalline, stony	33 Mixed crystalline and granular. Free from luster	33	Mixed crystalline and granular. Free from luster	134	32
											As forged	20.3	38.6	17.0	20.0	Uneven, coarse, crystalline, stony	51 Mixed crystalline, granular. Free from luster	51	Mixed crystalline, granular. Free from luster	143	34
AN	70.00	21.50	4.50	4.00	69.42	21.78	4.93	3.77	0.10	As cast	As cast	15.90	33.90	13.00	18.30	Fine, granular, shallow semi-cup and cone, silky edges	43 Fine, granular, silky edges	43	Fine, granular, silky edges	129	30
										As forged	As forged	25.40	39.80	21.00	24.50	Fine, granular, semi-cup and cone silky edges. Indications of having been worked too cold	53 Fine, granular, silky edges	53	Fine, granular, silky edges	148	34

TABLE 11.—*Effect of Iron on Aluminum Brass*

Series No.	Intended Composition					Actual Composition					Physical Condition	Yield Point, Tons per Square Inch	Maximum Stress, Tons per Square Inch	Elongation, Per Cent. in 2 Inches	Reduction of Area, Per Cent.	Fracture	Impact Number	Fracture	Brinell Hardness Number	Crystal Grains per Square Centimeter
	Copper, Per Cent.	Zinc, Per Cent.	Aluminum, Per Cent.	Iron, Per Cent.	Lead, Per Cent.	Copper, Per Cent.	Zinc, Per Cent.	Aluminum, Per Cent.	Iron, Per Cent.	Lead, Per Cent.										
6	59 00 38 00 3 00 Nil	58 85 38 55 3 10 Nil	As cast	20 50 38 6 19 00 21 50	Coarse crystalline, deep reddish color. Intercrystalline along the 2-in. parallel.	30	Coarse crystalline, reddish color.	148	152											
			As forged	18 50 43 00 29 00 33 50	Flaky, coarse crystalline, deep reddish color. Trace of intercrystallinity	69	Fine crystalline, marked reddish hue	159	2555											
AF ₂	59 00 37 50 3 00 0 50	59 10 37 31 2 96 0 61 0 02	As cast	21 00 40 40 19 00 15 00	Oblique, uniform, coarse crystalline. Reddish color	31	Coarse, crystalline. Reddish color	159	173											
			As forged	16 80 35 00 23 00 24 60	Light reddish yellow. Flaky crystalline. Free from intercrystallinity	63	Coarse crystalline. Reddish hue	159	4400											
AF ₂	59 00 37 00 3 00 1 00	59 00 37 00 3 00 1 00 Nil	As cast	21 30 43 20 26 00 27 60	Oblique, reddish color, crystalline, slightly intercrystallinity along the 2-in. parallel	38	Reddish yellow crystalline	159	1195											
			As forged	21 40 42 90 33 00 41 90	Fine crystalline, even, free from luster, silky edges	46	Very fine crystalline reddish color, free from luster	159	2015											
AF ₁	59 00 36 00 3 00 2 00	59 15 35 96 3 02 1 87 Nil	As cast	18 70 43 00 20 50 18 30	Oblique, reddish color, finely crystalline	22	Reddish oblique finely crystalline.	154	2220											
			As forged	20 00 38 00 35 00 47 20	Pale brown, granular, semi-cup and cone, silky edges. Free from intercrystallinity along the 2-in. parallel	67	Fine reddish brown granular, trace of silky edges	154	600											

As Forged.—Apart from a slight improvement in the ductility, the mechanical properties are not changed materially.

Alloy AF₁

As Cast.—By increasing the iron to 1.87 per cent., the effect has been to reduce the ductility and impact strength.

As Forged.—It behaves in every way similarly to alloy AF₃, except that the yield point has been increased.

Microstructure.—The structural changes due to the presence of iron both in the as-cast and forged conditions are similar to those found in ordinary brass and fully bear out the comments made. No satisfactory explanation can be offered of the fall in tenacity of alloys AF₃ and AF₁ by forging. These conflicting results are encountered frequently in beta brasses of this class and the cause is a problem for future research.

NICKEL IRON ALUMINUM BRASSES

In this series, the nickel and iron may be introduced by means of pure nickel and a 10 per cent. iron, copper-iron alloy, or by means of an alloy containing 10 per cent. iron, 10 to 20 per cent. nickel and 70 to 80 per cent. copper. The high-melting-point alloys should be melted down with the copper under charcoal, a little common salt stirred in and the zinc worked in last.

Quantities of up to 1.0 per cent. of iron show a slight all-round improvement of the mechanical properties of alloys AN₃ (Table 8) and AN₁ (Table 9) although its value here lies mainly in enabling the production of dense sand castings of any dimension where special strength and ductility are of importance.

As Cast.—The effect of 1.5 per cent. iron on alloy AN₂ is shown by alloy ANF₁, Table 12, this quantity appearing to exert much the same effect as 1.0 per cent. of iron on alloy AN₁, improving the strength, ductility and shock-resisting properties.

As Forged.—There is little to choose between the two alloys, although alloy ANF₁ still maintains a superior impact strength. It is an alloy which proves particularly useful where such a yield point and strength are required.

Structure.—The effect of the iron has been to increase slightly the quantity of the alpha constituent and to refine the grain still more. This is particularly noticeable in the cast condition, while as forged or heat treated, it has the structure of a heat-treated nickel-chrome steel.

NICKEL ALUMINUM TIN BRASS

Although it is common practice to introduce small quantities of tin into many of the special complex brasses, any advantage is conjectural.

TABLE 12.—*Nickel Iron Aluminum Brass*

Series No.	Intended Composition					Actual Composition					Physical Condition	Yield Point, Tons per Square Inch	Maximum Stress, Tons per Square Inch	Elongation, Per Cent, in 2 Inches	Reduction of Area, Per Cent	Fracture	Impact Number	Fracture	Brinell Hardness	Scleroscope Hardness
	Copper, Per Cent.	Zinc, Per Cent.	Aluminum, Per Cent.	Nickel, Per Cent.	Iron, Per Cent.	Copper, Per Cent.	Zinc, Per Cent.	Aluminum, Per Cent.	Nickel, Per Cent.	Iron, Per Cent.										
AN ₂	59 00 34 00	4 00	3 00			58 95 33 57	3 95	3 13	0 40	As cast As forged	26 00 27 40	42 50 46 70	6 00 11 00	8 40 11 70	Short, fine, stony, crystalline Short, fine, stony, crystalline	7 7	Short, fine granular Short, fine granular	185 200	30 45	2840 2907
ANF ₁	59 00 32 50	4 00	3 00			59 00 31 45	4 10	3 00	1 45	As cast As forged	23 40 24 30	44 50 45 80	12 00 16 00	15 00 18 30	Fine, close granular, earthy fracture Fine, close grained, stony	11 19	Fine, earthy, short Fine, earthy, short	159 185	27 29	

TABLE 13.—*Nickel Tin Aluminum Brass*

Series No.	Intended Composition					Actual Composition					Physical Condition	Yield Point, Tons per Square Inch	Maximum Stress, Tons per Square Inch	Elongation, Per Cent, in 2 Inches	Reduction on Area, Per Cent	Fracture	Impact Number	Brinell Hardness Number	Scleroscope Hardness Number
	Copper, Per Cent.	Zinc, Per Cent.	Aluminum, Per Cent.	Nickel, Per Cent.	Tin, Per Cent.	Copper, Per Cent.	Zinc, Per Cent.	Aluminum, Per Cent.	Nickel, Per Cent.	Tin, Per Cent.									
AN ₁	60 0 34 0	3 00	3 00	2 96	Nil.	60 5 33 65 2 89	2 88	2 96	Nil.	As cast As forged	16 60 21 00	36 70 39 80	19 0 28 0	21 5 33 5	Fine, stony, semi-cup and cone Free from intercrystallinity, fine, granular, silky edges, uneven	27 41	Fine, stony, short Fine, stony, slight silky tinge	125 148	18 27
AN ₂	59 25 34 00	3 00	3 00	0 75	0 15	59 06 34 68 3 28	3 28	0 75	0 15	As cast As forged	23 60 24 80	37 00 43 80	4 50 20 00	8 40 23 00	Short, fine, stony, exhibiting minute definite crystals Stony, granular, shallow cup and cone	9 39	Stony, very fine but definitely crystalline Fine, granular	154 165	34 41

From an extensive investigation on the influence of tin on aluminum, aluminum-manganese and other complex brasses, no evidence has been obtained to indicate that the presence of tin in small quantities improved the casting of the metal or the mechanical properties, either in the cold or hot state; nor does it seem to affect the corrosion-resisting power. If it exerts any influence at all, it is to give a slight improvement to the elastic properties.

Reducing the copper content of alloy AN₁ to 59 per cent. and retaining the nickel and aluminum constant at 3 per cent, small quantities of tin are deleterious to the physical properties; the effect of 0.75 per cent. tin is shown by alloy AN₅, Table 13.



FIG. 11.—As cast Cu 59.25, Zn 34.00, Al 3.00, Ni 3.00, Sn 0.75

Structure.—Figs. 11 and 12 illustrate the microstructure of alloy AN₅ in the cast and forged conditions. The disposition of the alpha constituent as thin boundaries around crystal grains consisting mainly of the beta constituent, explain the poor ductility and low impact properties. Forging having eliminated this structural weakness and replaced it by an exceedingly homogeneous close-grained one, explains the remarkable improvement in the physical properties that have been wrought by mechanical work.

This example, together with those previously referred to in this paper, fully demonstrates that the full possibilities and development of any particular alloy or series of alloys is only possible when considered in close conjunction with the disposition of the microconstituents.

Before concluding this section, attention should be drawn to the yield-point figures given, which appear in some instances to be both erratic and contradictory. In considering the elastic properties of brass, however, it must be remembered that there is no uniform relation between the proportional limit and the yield point, and that from the ordinary extensometer diagram, it is difficult to locate where the elastic state ends and the plastic state begins, or even make a satisfactory comparison of the form of the curves of one alloy with that of another. The yield point figures given² indicate the stress to produce a permanent set of 0.01 in. in a 2-in. gage length, and nothing more. They have been

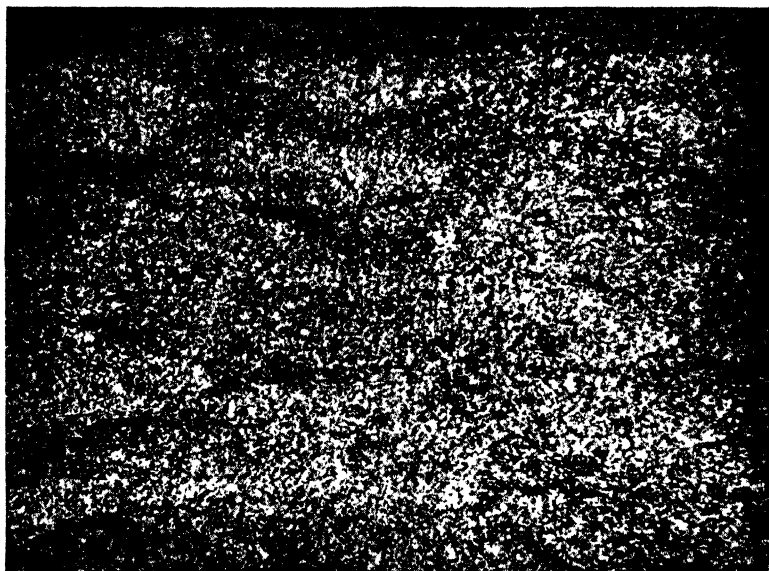


FIG. 12 —As FORGED Cu 59.25, Zn 34.00, Al 3.00, Ni 3.00, Sn 0.75.

included because of their common insertion by the engineer in his specification, although some form of dynamic stress test would serve his purpose better.

IMPURITIES

The question of impurities in brass of any kind is problematic. The difficulty is to differentiate between impurities that are harmful and those that are not. Lead, while commonly responsible for low test results, local weaknesses in castings, forgings and stampings due to segregation, patchy appearance of castings and the like, is actually an asset in quan-

² The tons referred to for both yield point and maximum-stress figures are gross tons, 2240 lb.

ties up to 0.70 per cent., if homogeneously distributed, both reducing cost and facilitating machining without affecting the physical properties. On the other hand, tin, aluminum, iron, nickel, vanadium and such special elements of proved value may come under the heading of "harmful impurities," if present unintentionally or incorrectly alloyed. Arsenic, cadmium, antimony and bismuth are among the most dangerous impurities in brass, but while small quantities of these might be harmful singly, they may not be objectionable if in combination with one another or with some other particular element.

Possibly the most objectionable impurity in high-strength brass, and one that does not receive the attention it deserves, is silicon. In no instance has the author found its presence advantageous, small quantities being conducive to brittleness without conferring any other useful property to compensate for the loss in ductility. It is one of the principal hardeners, and is twice as effective as aluminum, and ten times as effective as zinc, weight for weight.

The real value of silicon to the brass founder is as a deoxidizer. It should be used in the same way as magnesium and phosphorus, which are among the best scavengers, but harmful if any remains in the finished alloy. Magnesium exerts a similar effect to silicon. Phosphorus, if present in quantities over 0.15 per cent., causes both blistering and honeycombing. Carbon monoxide, sulfur dioxide, nitrogen, hydrogen, and various hydrocarbon gases are present in all brass, sound and unsound. If the charge is overheated or directly contaminated by obnoxious fumes, the fumes are absorbed in excessive quantities, and their evolution on cooling is the principal cause of blowholes in castings.

PROBLEMS OF MANUFACTURE

Melting.—Briefly stated, the principal features to be observed in melting are:

1. Prepare suitable stock alloys for the introduction of the more refractory metals.
2. Carefully select materials, calculating the mixtures from their actual chemical composition and allowing for melting losses.
3. Carefully weigh out the necessary additions and charge in their correct order.
4. Avoid the use of scrap of doubtful chemical composition, particularly with regard to iron, aluminum, tin, silicon and dross contamination.
5. Melt as rapidly as possible in a neutral or slightly reducing atmosphere, but never superheat more than 20 per cent. of the actual melting temperature, and control pyrometrically.
6. Avoid retention in the furnace for long periods after correctly melting. Where this is impossible, carefully control the temperature, cover with a protecting slag and adjust for zinc losses.

7. Mix well, but do not oxidize in so doing.

8. Deoxidize with a little phosphor-copper or phosphor-tin just before casting if the alloy contains manganese; if manganese is absent, as in the nickel aluminum iron brasses, a little copper-manganese is beneficial both as a deoxidant and desulfurizer.

9. Avoid, as far as possible, contamination with slag in the ladle.

Crucible Melting

When melting in the crucible, no difficulties are met other than those mentioned in the preparation of the development alloys. Despite the high cost of fuel and crucibles, this is the method most commonly used, and is favored because of the flexibility of temperature control, the ease of mixing, low melting losses and protection from dirt and obnoxious gases during melting.

At the same time, the open-hearth furnace is of particular value for the manufacture of large castings. Where first cost permits, the gas producer regenerator or recuperator type is recommended. It is flexible, economical and efficient. The coal-fired open-hearth furnace is commonly installed, but it is costly to run, and both the temperature and composition of the metal are difficult to control.

The thermal efficiency of the oil-fired open-hearth furnace is, roughly, about twice that of the ordinary coal-fired air furnace. Lighters-up, furnacemen and ash removers are dispensed with and the flexibility of control of the furnace is a great advantage. The fierceness of the oil-flame is a disadvantage to this furnace, although by the aid of a burner, permitting accurate regulation of both oil and air, and by the use of a good fuel oil, no trouble should be encountered in this direction.

The common objection to all open-hearth furnaces for the melting of special brasses is the large surface of metal exposed to the furnace gases, which, if oxidizing or sulfurous in nature, are injurious. A few logs of hardwood charged during the melting-down period, an occasional shovelful of hardwood charcoal or anthracite, and a suitable protecting flux, remedy this. The choice of the flux is extensive, but either of the following may be recommended:

1. Equal parts by weight of plaster of paris and fluorspar;

2. Soda ash, 30 parts; fine silica sand, 20 parts; fluorspar, 33 parts; borax, 17 parts, by weight. These should be ground down, 2 to 3 per cent. by weight of the charge being sufficient. Melting should not be forced.

Electric Furnace

This is the ideal melting furnace so far as quality of metal is concerned. With either the direct or indirect resistance or induction furnace, melting is almost automatic, zinc losses and impurity contamination are reduced

to a minimum, and the melting temperature is under control. The crucible resistance furnace is a useful melting unit, but it is costly in both crucibles and current. The induction furnace is flexible but costly in fuel consumption. The indirect arc rocking furnace, possessing the advantages of both the indirect resistance and induction, without the accompanying high melting costs, holds out greatest promise.

Scrap

For high-grade castings only approved scrap should be used. Where the chemical composition is uncertain, and when the metal is either of undesirable form or dirty, the scrap should be run down into pigs. In the recovery of brass swarf, all scrap contaminated with white metal and excessive oxide should be thrown to one side, and the remainder passed through a magnetic separator. If briquetting is possible, 2 to 3 per cent. of borax or plaster of paris should be mixed in and sprinkled with water immediately before pressing. If this procedure is not possible, the swarf should be mixed with 3 to 5 per cent. plaster of paris or 5 per cent. of the No. 2 flux mixture given above, together with a little coal dust, and melted with a reducing flame.

The objection to the use of fluxes in the open-hearth furnace lined with ganister is the accumulation of slag which banks up the hearth and puts the furnace out of commission. To avoid this, the bottom should be flowed with a suitable flux such as plaster of paris or this material in conjunction with soda ash and fluorspar, according to the nature of the slag.

Casting

Ingots and Chill Castings.—Ingot molds should be short and squat rather than long and thin, and slightly wider at the top than at the bottom. Both ingot molds and chill molds should be preheated to a temperature of 37° to 93° C., cleaned with a steel brush and dressed with an organic material. When a clean, smooth skin is desired, a simple tallow or heavy mineral-oil dressing is recommended. For general work, a facing of tar followed by a mixture of dark cylinder oil of over 205° C. flash point and powdered charcoal, and this followed by a dusting of fine charcoal. Polishing-in of black lead or smoking with burning resin or creosote oil is quite satisfactory for ingots, and does not give off obnoxious fumes and flames common to oil and tar dressings.

Speaking generally, 10 per cent. superheat is a satisfactory casting temperature, although for heavy ingots it may be reduced to 7 per cent. Top-pouring through a specially prepared runner basin is recommended. A refractory head is an advantage, but not essential, if the caster understands his job. For the manufacture of high-class stampings or sheet, machining the skin of the ingot or slab may be found advantageous.

Green Sand, Dry Sand and Loam Castings.—The success in the manufacture of any brass casting mainly depends on the selection of the correct molding materials and the skill of the molder. Briefly stated, the technical properties to be controlled in a molding sand are: (1) Bond, *i. e.*, strength; (2) grain size or texture; (3) heat conductivity; (4) refractoriness; (5) permeability and longevity. Having once established a means to control and standardize the mixtures for the various classes of work, many of the molder's problems automatically disappear, and the economies effected soon compensate for the initial expenditure necessary. In green-sand molding, alone, the preparation of a synthetic molding sand has effected an appreciable saving.

Conditions governing the choice of mold—green, dry sand or loam—and the general principles of molding, are very similar to those of ordinary brass castings, and call for no special comment.

Gating and Feeding.—Without doubt, these are the cardinal problems of the molder. Wrong gating and feeding are responsible for more defective work than any other operation in the foundry. They call for an elementary knowledge of both physics and mechanics, together with practical experience, without which, it is impossible to make a commercial casting, *i. e.*, a good quality casting for the minimum expenditure of time, labor and materials. It is folly to attempt to lay down hard and fast rules, as almost every class of casting presents its own difficulties.

The principal points to be observed in gating and the fixing of risers are:

1. To fill the mold so that the stream of metal is continuous and not broken up on entering the mold. Wherever possible run from the bottom or on the level with a good head. This is particularly important in brasses containing aluminum and manganese, which must be cast under the exclusion of air as far as possible.

2. To prevent dross from entering the mold: For flat, circular castings, a whirl gate is preferable; for cylinders and the like run from the bottom by means of a series of tangentially cut V-shaped jets; and for general castings, an ordinary skim gate.

3. To arrange for a straight run of the metal and to avoid direct contracting on delicate cores or projections in the mold. (Avoid sharp angles at turning points.)

Feeding.—1. Mold in such a way that the heavy sections are placed in the upper part of the mold.

2. Connect the heavy sections, which are shut off from the lighter sections, to a good feeding riser, by a section of increasing dimensions.

3. Use chills on the thicker sections to equalize the rate of cooling.

4. Use risers or flows of conical form appreciably larger at the top than the thickest section of the job.

5. Place risers at the highest point of the castings and directly above the thickest sections.

6. It is false economy to cut down the number or size of the risers, and small dummy risers should be placed where dirt is likely to be trapped.

7. Risers should be filled preferably with hot metal from another ladle or crucible.

8. Where rod feeding is necessary, choose the right section of rod and preheat before immersing.

Pouring Dishes.—These should be designed so that bottom pouring is always obtained, thus preventing the entrance of scum into the mold. To this end, deep pouring dishes and cast-iron plugs are an advantage. For large important castings, the pouring dishes should hold at least one-third the weight of the casting.

Pouring.—In the final operation of pouring, the first and foremost factor controlling the production of sound castings is the selection of the correct casting temperature from the dimensions and requirements of the job. Never cast with less than 6 per cent. superheat, nor more than 15 per cent.

The casting temperature of these alloys usually ranges between 930° C. to 1030° C., according to the chemical composition, etc. The actual casting temperature, however, is best found from the copper-zinc constitutional diagram, adding the desired percentage of superheat to the melting point figure. For actual foundry use, small quantities of special metals (under 0.5 per cent.) need not be taken into account. Exceeding this amount, they should be calculated back into either their copper or zinc equivalents. When the alloy is complex, an actual freezing temperature determination is the only satisfactory method. If cast with metal on the cold side, short runs, low strength, brittleness, drawing, blowholes, cracks and mechanically contaminated oxide are the principal defects encountered. If too hot, there will result honey-combing, wrong composition, poor physical tests, weak crystal zones and segregation.

The Cracking of the Nickel Silvers in the Course of Annealing

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(Syracuse Meeting, October, 1925)

DURING the heating of cold-worked nickel silver, the tendency of the material to crack is well known. The present research deals with this question, and may conveniently be divided into the following sections: Changes in these alloys during heating and cooling, determination of the temperature at which cracking occurs, effect of grain size, quenching cracks, methods of overcoming annealing cracking. The work is far from complete, in particular the influence of impurities on this tendency has not been investigated, but the results so far obtained lead to certain definite conclusions, which are of theoretical and practical importance.

CHANGES IN ALLOYS DURING HEATING AND COOLING

During the annealing of many metals at a temperature just below that at which recrystallization sets in, there is evidence of some change, the effect of which is to harden and embrittle the material. This effect has been most clearly demonstrated in the cases of aluminum, copper, brass, and nickel silver, and appears to be a common property of cold-worked metals and alloys, or, at any rate, the non-ferrous ones. The effect would obviously offer an explanation for certain types of annealing cracking, but the trouble is so much more common in the nickel silvers than in the other alloys that some special cause should be looked for. There is, however, fairly good reason for believing that similar cracking may occur in some of the brasses; D. Bunting¹ suggests that the α brasses toward the saturation limit are subject to a transformation closely allied in nature to that known to occur in the nickel silvers at around 320° C.

Although the existence of this critical temperature range was known, it did not necessarily follow that this transformation was responsible for the trouble under investigation, so the first portion of this paper deals with the attempts made to determine whether other critical changes might not occur in these alloys. There were already reasons for the belief that such would prove to be the case, as the mechanical properties of the nickel

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¹ *Jnl. Inst. of Met.* (1924) 1.

alloys that have been annealed after cold work certainly do not, in most cases, lie on smooth curves when plotted against the temperature.

The two properties selected for this part of the work were the electrical resistance and the linear coefficient of thermal expansion. The latter is clearly important, for if there are sudden changes of volume in the material at a definite temperature, there must be accompanying developments of the internal stress, which might be responsible for the formation of cracks. The results obtained indicate fairly definite critical temperatures at 320° C. and 425° C., as well as others at higher temperatures. As it is well established that cracking occurs below visible red heat, it would appear that one or both the points mentioned are possible causes of failure, so the next aspect of the work was the determination of the exact cracking temperature.

DETERMINATION OF CRACKING TEMPERATURE

The first series of experiments was conducted on rings cut from cups spun from sheets containing from 11 to 20 per cent. of nickel. A thermocouple was attached to the ring by means of asbestos thread and the heating, which was as rapid as possible, was effected in a gas-fired, muffle furnace. Even when deeply notched, to localize the stress, none of these rings could be induced to crack, a fact probably to be ascribed to the effect of the parting from the original cup, or to the manner in which the heating was effected. From results obtained later, there appears to be little doubt that both factors were operative; although for the purpose for which the experiments were initiated the results were purely negative, they did throw light of considerable value on the means of the inhibition of the trouble.

In another series of tests, attempts were made to induce cracking in the spun cups themselves, the belief being that, even when rings were parted with a sharp tool, vibratory stresses were set up that had an effect similar to that of springing, or malleting in equalizing the cold-working stresses and so preventing the formation of cracks. Here again the results were largely negative; although many of the cups did not crack, all the failures occurred in the temperature range 349° C.-390° C. Once this range was exceeded trouble from this cause ceased. There is, however, a point of considerable practical importance that arises from these results. The cups were specially prepared for this work by Messrs. James Dixon & Sons., Ltd., Sheffield, and were severely treated in the spinning, being taken very much further without annealing than would normally be the case and they were spun on iron chucks further to increase the liability to crack. There can be no doubt that all these cups would have cracked had the annealing been normally conducted in the flame of the blow-lamp; it appears, therefore, that muffle annealing is much less likely to produce failure than is open heating in the blow-lamp.

The greater liability, in the latter case, may be due to more rapid heating—which may also be local—or alternatively to the increased liability to oxidation.

Local annealing, while adjacent portions remain hard, is obviously likely to lead to cracking; there is also good reason for the belief that an oxidizing atmosphere tends to produce a similar result. For example, in one establishment, seriously troubled by fire-cracking, the rebuilding of the annealing furnaces so that the flame ceased to come into contact with the metal practically eliminated the trouble.

RECRYSTALLIZATION AND GRAIN GROWTH

As the temperature just determined at which cracking takes place is in the neighborhood in which the recrystallization also occurs during the heating, it was felt that work on the grain growth would not be without interest. Measurements were made of the average size of the crystal grains for material subjected to progressively increasing amounts of cold work and annealed at definite temperatures for a given length of time. The materials used were three grades of nickel silver, the analyses of which are given in Table 1, and in each about 250 crystals, on the average, were included in the measured area.

TABLE 1

	10 Per Cent Nickel Alloy	15 Per Cent Nickel Alloy	20 Per Cent Nickel Alloy
Copper..	61 25	62 06	64 82
Zinc....	27 42	22 73	15 83
Nickel..	10 55	14 81	19 03
Iron.....	0 35	0 20	0 27
Lead...	0 38	Nil	Nil
Manganese	Trace	0 09	0 03

Being originally in the cold-worked state, the strips were first softened at 600° C., for $\frac{1}{4}$ hr., and cooled in the muffle. They were then rolled in a set of hand rolls in such a manner that for each composition increasing amounts of reduction in thickness from 0 to 80 per cent. were obtained. This was done by rolling the strips together with a hard-steel wedge-shaped plate about 8 in. long, 2 in. wide. This arrangement is illustrated in Fig. 1. On one strip, such a rolling would reduce the thickness from 0 per cent. at one end to over 20 per cent. at the other. To obtain reductions in thickness from 20 per cent. to over 40 per cent., the annealed strip was first straight rolled down to a reduction of 20 per cent. and then taper rolled from 20 to 40 per cent. The higher reductions were produced by straight rolling to near the lowest value required on the strip, followed by taper rolling the remaining 20, or so, per cent. Roughly speaking,

every inch along the specimen corresponded to a reduction in thickness of about 10 per cent. Two sets were then close annealed at 730°C ., the time in one case being $\frac{1}{2}$ hr. and in the other $3\frac{1}{2}$ hr., and cooled in the closed muffle. The results are given in Table 2 and plotted in Fig. 2.

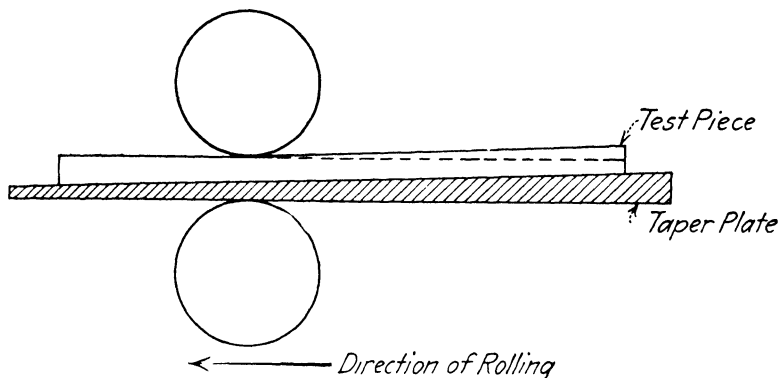


FIG. 1.—METHOD OF TAPER ROLLING.

The first point to be noticed is the effect of the nickel content on the grain size; the greater the amount of nickel the smaller the crystals. The graphs of the results after annealing for $\frac{1}{2}$ hr. and $3\frac{1}{2}$ hr. show that

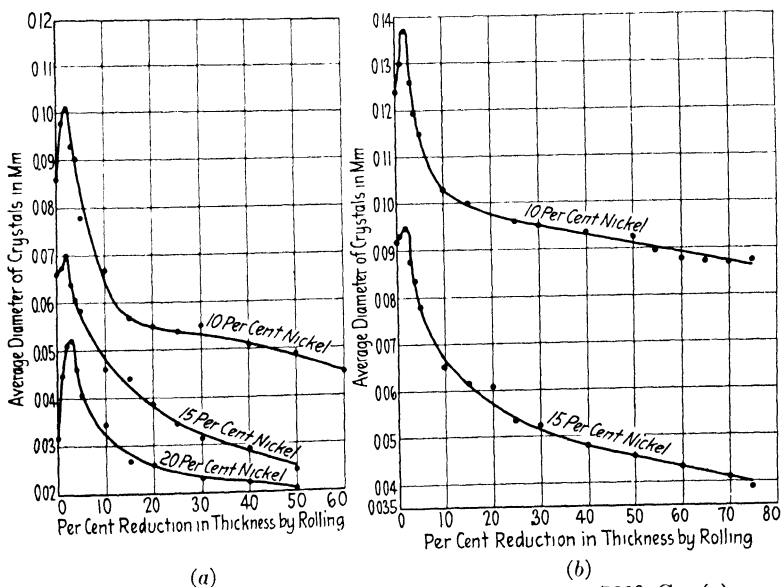


FIG. 2.—GRAIN GROWTH AT ANNEALING TEMPERATURE OF 730°C .; (a) TIME OF ANNEALING $\frac{1}{2}$ HR., (b) TIME OF ANNEALING $3\frac{1}{2}$ HR.

the size of the grains is little greater in the latter case than in the former. An important point is the exaggerated grain growth due to annealing after too slight stressing, the maximum appearing when the specimens had

received an amount of cold work corresponding to a reduction in thickness by rolling of about 2 per cent. From the excessive grain growth at 2 per cent., the curves fall rapidly to about 15 per cent., beyond which the decrease in grain size due to increasing amounts of rolling is quite small.

TABLE 2.—*Annealing Temperature 730° C.*

Per Cent. Reduction by Rolling	Average Diameter of Crystals, in Millimeters				
	Time of Annealing $\frac{1}{2}$ Hr.			Time of Annealing $3\frac{1}{2}$ Hr.	
	10 Per Cent. Nickel	15 Per Cent. Nickel	20 Per Cent. Nickel	10 Per Cent. Nickel	15 Per Cent. Nickel
0	0 086	0 0662	0 0319	0 124	0 092
1	0.098	0 0675	0.0450	0 130	0 093
2	0.101	0.0702	0 0511	0 137	0 095
3	0 093	0 0640	0 0522	0 126	0 0875
4	0 0905	0.0608	0 0462	0 1195	0 0835
5	0 078	0 0578	0 0408	0 115	0 078
10	0 067	0 0464	0 0346	0.103	0 0652
15	0 057	0 0441	0 0269	0 100	0 0616
20	0.055	0 0387	0 0261	0 1003	0 0611
25	0 054	0 0347		0 096	0 0533
30	0 055	0 0314	0 0230	0 095	0 0523
40	0 051	0 0292	0 0221	0 0935	0 048
50	0 049	0.0246	0 0206	0 0925	0 0457
55				0 0895	
60	0 045			0 0875	0 0433
65				0 0870	
70				0 0865	0 041
75				0 0870	0.039

In the commercial rolling of nickel-silver ingots, too slight a "nip" in the rolls is looked upon as being likely to cause trouble by cracking of the metal on subsequent annealing. This feature and exaggerated grain growth are probably correlated. With a slight nip, excessive crystal growth takes place on annealing and the material is prone to crack. However, on exceeding a definite pressure, a "critical reduction" in thickness is produced at which, on annealing, exaggerated grain growth gives place to normal grain growth, and failure by such cracking is avoided. This critical reduction in the case of nickel-silver alloys is about 15 to 20 per cent. The cracking of ingots on annealing after slight cold rolling is probably the result of the difference in grain growth between the surface layers and the center of the ingot. Where the deformation has been most severe, *i. e.*, on the outside, small crystals are formed, while in the center of the ingot, where the cold work has been comparatively slight, the crystals remain small; but at some intermediate point a very coarse crystalli-

zation is found. The locality of the coarse crystallization is dependent on the exact amount of reduction and the roll diameter in relation to the thickness of the alloys.



FIG. 3.—CRACKED ERICHSEN TEST SHEET: COPPER 63.61 PER CENT., ZINC 15.99 PER CENT., NICKEL 19.17 PER CENT.



FIG. 4.—CRACKED SPOON BLANK.

CRACKING DURING COOLING

So far two types of cracking have been discussed, namely the ordinary annealing cracking of cold-worked material and the cracking of ingots on which too little cold work has been imposed. Although these

two classes may have one common origin, there are sufficient points of difference to justify their differentiation. A third type of cracking, however, is distinct from either. During the preparation of a series of samples for Erichsen tests, from different grades of alloy, cracked specimens were found only in the case of those quenched from the annealing temperature; and of these only in the case of the highest nickel content, namely 20 per cent. It is clear from this, and from other evidence, that the rate of cooling exerts a marked influence on a certain type of cracking, and that in the case of high-nickel alloys anything of the nature of a quenching may lead to serious trouble. Quenching cracks were found, however, only in the cases where the temperature of quenching had

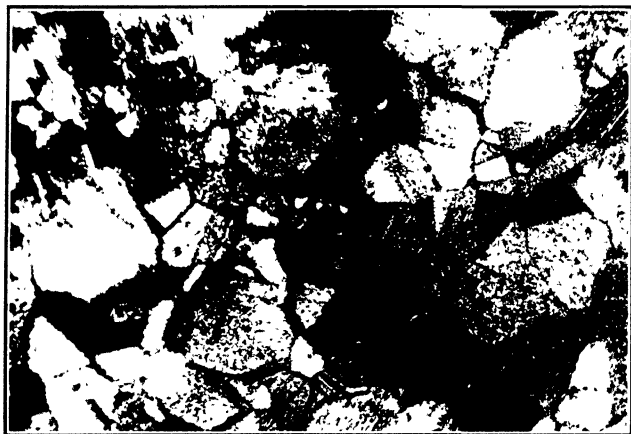


FIG. 5.—FIRE-CRACK.

exceeded 600°C . The cracked test sheet, 0.036 in. thick, quenched from 850°C . is shown in Fig. 3. The two cracks present distinctive features, and represent two different types. The first type, represented by the broad crack running horizontally across the specimen, is the true annealing or "fire-crack," of which another example is shown in Fig. 4. On examination this fracture was found to be intercrystalline and badly oxidized (see Fig. 5). The position of the annealing crack in the spoon blank is interesting. The original thickness of several cracked spoon blanks was measured by a pointed micrometer, together with the thickness at the crack. It was found that, as a rule, the fracture occurred at a reduction corresponding to that at which the small grains give place to grains of rapidly increasing size, indicating the effect of the recrystallization.

The second type of crack, represented in Fig. 3, by the fracture extending inwards from the upper edge of the test piece, is from an entirely different cause. Like the "fire-crack," this cooling crack is intercrystalline, as shown in Fig. 6. The characteristic distinguishing

feature between the two types of cracks is that, while the fracture caused by fire-cracking is oxidized, the fracture of a cooling crack is quite bright. With much of the material supplied for this research, although the production of fire-cracks was a matter of the greatest difficulty, quenching cracks could be produced at will provided that the nickel contents were sufficiently high and that the materials were quenched sufficiently rapidly from a sufficiently high temperature. It is evident that the conditions, such for instance as composition, which render a certain material more or less immune from fire-cracking do not inhibit the formation of the quench-



FIG. 6.—COOLING CRACK.

ing cracks. The further interesting observation was made that for both quenching and annealing cracking badly overheated or burnt material was much more prone to fail than was material of which the previous annealing had been satisfactory.

EFFECT OF LOW-TEMPERATURE ANNEALING ON INTERNAL STRESS

The work of Moore and Beckinsale on the removal of internal stress in cold-worked brass suggested that an investigation on similar lines would be of interest in connection with the nickel silvers. There can be little doubt that internal stress is responsible for the cracking during annealing, and if it were possible to reduce this stress until it became inoperative cracking would be eliminated.

One big difficulty experienced in the earlier stages of this work was the impossibility of obtaining material of which the initial stress was constant. It was soon seen that although the general type of curve obtained when the residual internal stress was plotted against the annealing temperature was constant, the numerical value of the stress left after a prescribed treatment was dependent on the actual value of the initial stress. In

the 20 per cent. nickel alloy annealed at 270° C. for 2 hr., the residual stress after this treatment in relation to the original stress was:

Original stress, tons per sq. in	20 2	16 2	13 9
Residual stress, tons per sq. in.....	15 0	10 6	8 3

In these cases, the original stress was the only variable factor.

The method finally adopted for this branch of the work, using material of which the analyses in Table 3 are typical, was as follows:

TABLE 3.—*Analyses of Nickel Silvers*

	Grade A, Per Cent.	Grade B, Per Cent.	Grade C, Per Cent.
Copper	61 65	65 50	60 40
Nickel.	11 79	16 28	20 64
Zinc..	26 02	16 30	19 34
Tin	0 126	0 094	0 095
Lead...	0 05	0 04	0 03
Manganese.	0 05	0 06	0 04
Iron ..	0 05	0 07	0 07
Sulfur.	0 04	0 04	0 03
Carbon .	0 10	0 11	0 08

After carefully measuring the dimensions of the spun ring as received, the ring was cut at one point, with shears, and the new curvature obtained. Two small drill holes (50 gauge) were made, one at each end of the strip and the ends fastened together by means of soft-brass rivets. The position of the rivet holes was arranged so that when completed the ring would fit easily into a 3-in. diameter vertical electric furnace in which the heat treatments were carried out. From the dimensions of the riveted ring and the change in curvature, it is possible to calculate the tensional stress in the outer edge of the ring.

When the furnace was steady at the required temperature, one ring from each of the series was introduced for a definite period of time, removed, cooled in air, and then opened by filing off the head of the rivet. The new curvature was obtained by tracing the curve and obtaining the mean of four diameters. The rings were then re-riveted, replaced in the furnace for a further definite period of time and the curvature and stresses again obtained. This process was repeated until either no further reduction in stress was obtained or the stress was only very slight.

As re-riveting strained the ring to the same curvature that it possessed before the rivet had been removed, we assumed that this process placed the ring under the same stress as before and that, therefore, the time factor could be considered as additive. That this assumption is only an approximation and cannot be used without introducing some error

is obvious, but the limitations of the material available made it necessary to use some such intermittent method. The resulting smooth curves obtained by plotting stresses against temperature show that the errors are only slight, and yield interesting information as to the influence of time and temperature on the reduction of stress.

The experiments were carried out approximately at 25° C. intervals over the range 200°-300° C. and the results are given in Table 4 and in Fig. 7.

TABLE 4

Annealing Temperature, Degrees C	Time, Hours	Residual Internal Stress, Tons per Square Inch		
		11 Per Cent. Nickel	16 Per Cent Nickel	20 Per Cent Nickel
180	Initial stress	17 27	33.83	16.28
	1	11 48	15 73	12 04
	2	10 75	14 41	9 99
	3	10 38	12 35	9 57
	4	10 17	12 0	9 28
	6	10 09	11 5	9 25
225	Initial stress	17 55	24.4	23 4
	1	11 58	11 8	13 1
	2	10 1	11 3	12 8
	3	9 7	11 2	12 7
	4		11 1	11 7
	6	9 6	10 8	
250	Initial stress	13 6	20 7	13 05
	$\frac{1}{4}$	10 1	13 2	11 3
	1	9 5	12 6	10 5
	2	9 3	12 3	10 4
	4	8 6	10 9	8 9
270	Initial stress	13 4	21 4	16 2
	2	7.1	9.2	10.6
300	Initial stress	18 4	10 7	11.0
	$\frac{1}{4}$	9 5	6 2	9 0
	$\frac{1}{2}$	8 8	6 2	9 2
	1	8 5	5 3	8 2
	2	8 0	4.7	7.7

The following formula, due to Stanfield, was used in calculating the tensional stress from the change of curvature:

$$S = \frac{E}{d} \frac{dd'}{d}$$

where S = stress; E = Young's modulus; and d, d' = diameters before and after annealing. The formula requires a knowledge of Young's modulus, therefore, as no accurate values were known, it was decided to make the determinations on the actual materials used.

Two rings from each material were carefully cut and straightened out as gently as possible; one of each was then tested in the cold-worked condition and the other after annealing. A Martens extensometer was used, the tensile stress applied being imposed in a Buckton machine. The values obtained were

Nickel, Per Cent.	Limit of Proportionality, Tons per Square Inch		Young's Modulus, Pounds per Square Inch $\times 10^7$	
	Annealed	Cold Worked	Annealed	Cold Worked
11	9 39	9 44	1 12	1 25
16	10 65	10 81	1.32	1 61
20	11.04	13 41	1 25	1 53

It will be noted that the values of the limit of proportionality have been included. No satisfactory values being generally available, it was thought well, during the determination of Young's modulus, to proceed to the determination of the elastic limit.

The tensile properties of nickel silvers at temperatures up to about 350° C. are of importance in connection with the foregoing experiments. W. H. Dearden, M. Sc., conducted the following tests on a 20 per cent. nickel alloy in the cold-rolled condition, when he obtained the following results.

TABLE 5

Temperature, Degrees C.	Limit of Proportionality, Tons per Square Inch	Maximum Stress, Tons per Square Inch	Elongation, Per Cent. in 2 In.	Modulus of Elasticity, Pounds Per Square Inch
200	11 9	28 4	25 5	2.22×10^7
270	12 8	28 8	24 0	2.02×10^7
340	9 9	28 3	23 5	1.85×10^7

The full analysis of the material examined was: Copper 61.5 per cent., zinc 17.1 per cent., nickel 20.8 per cent., iron 0.25 per cent., aluminum 0.29 per cent., tin 0.04 per cent.

An examination of the results of the annealing experiments show that the value of the residual stress appears to be practically independent of the nickel content, but to vary slightly with the initial stress. The curves for all these sets of determinations are closely alike, so only one, Fig. 7, is shown. The stress falls off rapidly at first, especially when the initial stress is unusually high, and at length becomes practically constant. In most cases, this asymptotic value is about 10 tons per square inch, or slightly lower.

As the maximum stress at these temperatures is about 28 tons per sq. in., it would appear to be very probable that such values of the internal stress would be innocuous and cracking would then be eliminated. The authors would suggest, therefore, that one of the readiest means of overcoming trouble resulting from fire-cracking is to preheat the material to a temperature below that at which the cracks are produced and to maintain it at that temperature for a period sufficiently long to eliminate the major portion of the stress. From the results here given, it would appear that a temperature of about 250°C . will produce this effect in about 1 hr. (once the temperature has been attained) or one of 300°C . in $\frac{1}{2}$ hr. As there is known to be a critical point in these alloys at 320°C ., it would probably be safer to conduct this preheating at a temperature not higher than 300°C . Dr. R. S. Hutton has shown that such a treat-

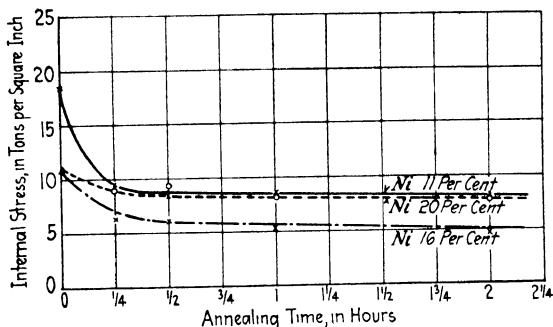


FIG. 7.—REDUCTION OF ANNEALING STRESS ON ANNEALING AT 300°C .

ment does appreciably reduce the liability to crack during subsequent heating. As a result of the low temperature required, the preheating could be done with the waste gases from the annealing furnace proper at a very small cost of both time and money.

When the annealing is conducted at a temperature higher than 300°C ., a curious effect was observed. The actual numerical values for these higher temperatures are rather less certain than those for the lower temperatures, as the initial stresses varied more than one would wish; but in view of the fact that at 300°C . the variation of residual stress with initial stress was of the order of 2 tons per sq. in. only, despite very large variations of the initial stress, it is reasonable to suppose that as the annealing temperature is raised the value mentioned (2 tons per sq. in.) may be taken as the probable maximum variation. The curves for all three materials were similar in shape, despite the fact that two sets of determinations were carried out—one merely taken up to the temperature and at once cooled and the other maintained at the temperature for $\frac{1}{2}$ hr. One set of results only need be given; these refer to the 16 per cent. nickel alloy heated for $\frac{1}{2}$ hr. (Fig. 8).

Temperature, degrees C.	Spun.	225	250	300	305	450	500	550
Internal stress, tons per sq. in.		22	12	12.5	5.5	22	17	1 nil

It will be noted that just above 300° C., there is a sudden marked increase of internal stress; this is exactly what would be expected from the knowledge that around that temperature a change sets in which profoundly affects the mechanical properties.

The stress in this particular series of measurements rises from a very small value to one of the order of the original stress in the spun material. It would appear to be nearly certain that the only possible ultimate cause of the fire-cracking is the fact that at the temperature of the cracking the internal stresses exceed the tensile strength. This may happen either by the latter falling while the stress remains more or less the same, or by the stress rising while the tensile strength remains essentially unaltered. It has been shown that up to 300° C. the stress falls appreciably, and equally clearly that the tensile strength is almost unaffected. The only

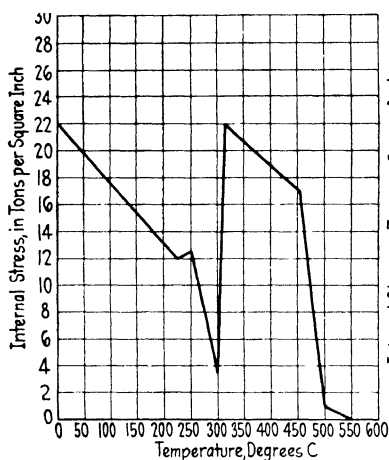


FIG. 8.—INFLUENCE OF TEMPERATURE ON INTERNAL STRESS; NICKEL SILVER, 16 PER CENT. NICKEL.

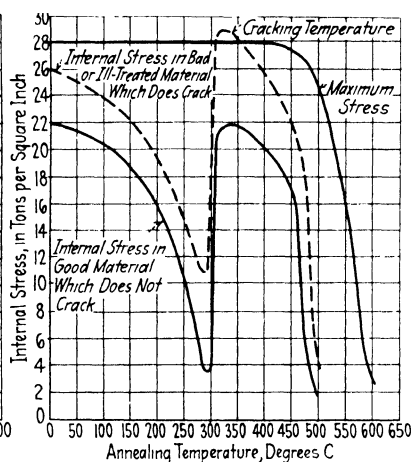


FIG. 9.—DIAGRAM EXPLAINING CAUSE OF FIRE-CRACKING.

conclusion that can be reached, therefore, is that at some temperature above 300° C. the internal stress rises again suddenly until it may exceed the tensile strength of the material when failure must occur. These simple arguments demand that some such effect as the rise actually demonstrated must inevitably take place.

A further point of importance in connection with this building up of internal stress above 300° C. is the effect of time. When rapidly heated up to the temperature, the internal stress is much higher than when the alloy is allowed to soak at the temperature. The following figures illustrate this effect. The 16 per cent. alloy, when rapidly heated to 450° C.

and not soaked, was stressed internally to the extent of 38 tons per sq. in., a value exceeding the maximum stress in pure tension; after soaking at that temperature, the stress was reduced to 17 tons per sq. in. At just over 300° C., for the 20 per cent. nickel material, the respective stresses were 31 and 25 tons per sq. in. It is clear that at such temperatures the material is stressed to within a very small range of the maximum stress and it is not difficult to realize that anything which is enabled to increase the internal stress will appreciably lower the chance of the material to withstand cracking. The fact that the rapid heating in the open flame of the blow-lamp is much more liable to crack the same material than is annealing in a closed muffle thus finds a rational explanation.

SUMMARY AND GENERAL OBSERVATIONS

It has been shown that nickel silvers may crack either during the heating or while cooling after annealing. The former is the usual fire-crack and is characterized by the fact that it is clearly oxidized. If the cooling rate is high, as in quenching, cracking may again occur; these cracks, however, are unoxidized and clean. Especially in the case of alloys of high nickel content is the trouble that may arise from cracking in quenching serious. It does not appear that the quenching crack is produced unless the temperature from which the material has been cooled has exceeded 600° C.

It has been shown that the typical fire-crack occurs at a temperature around 350° C. Probably the trouble is associated with the fact, discovered by Le Chatelier, that in these alloys a change takes place around 320° C. If this temperature is safely passed, the chances of cracking during further heating to a higher temperature are exceedingly small.

It has been shown that the conditions under which the specimen is heated exert a marked influence on the tendency to crack. The more gradual and uniform the heating, the less likelihood is there that the article will develop cracks. Contact with flame is liable to cause cracking. One manufacturer found that by close annealing in a muffle furnace there was much less wastage from this cause than occurred in furnaces in which the flame came into actual contact with metal being annealed. The same fact was clearly discerned in the work recorded on the temperature at which the cracks were formed. Cups of severely spun alloys that cracked with the utmost readiness when annealed in the flame of a blow-lamp resisted most obstinately to crack when heated in a muffle.

Other causes of increased tendency to crack are: (1) Impure metal, especially where there is much impurity in the form of inclusions of oxides, slag, graphite, lead, tin-bearing constituents, etc. Quite apart from chemical composition in the ordinary sense, "dirty" metal due to casting conditions is very likely to crack. The "non-cracking" nickel silvers are all very pure and it is to their chemical purity and careful melting and

casting that their special properties appear to be due. (2) Unequal stresses are a very common cause. This is specially found in cross-rolling where such inequality is inevitable; badly aligned rolls with worn surfaces also are a common cause. By careful attention to the rolls in one works, cracking was appreciably reduced.

It has been shown that in the annealing of nickel silver, the phenomenon of critical grain growth occurs. For a certain degree of deformation, very large crystals appear on annealing; while when the amount of work is greater or less the grain size is much smaller. Annealed cross-rolled spoon blanks show the effect well; and it is at least probable that this grain growth plays an important part in the cracking that occurs. The phenomenon is also the probable explanation of the well-known fact that ingots which have received too little reduction in breaking down before they are annealed tend to crack badly. The amount of reduction required to give the critical growth is quite small, about 2 per cent. reduction giving the coarsest structure. The shearing of blanks, and similar operations, always yield material near the surface that has received this critical deformation and which, therefore, on annealing will give excessively large crystals.

It has been shown, as Doctor Hutton first suggested, that an annealing at a low temperature, below that at which the cracks are formed, will reduce the internal stresses to such a limit that cracking will not occur. Further, such a treatment will tend to equalize the stresses with the result again that they will be less harmful. By heating the metal to 250° C. and by keeping it at that temperature for about 1 hr. the stresses are reduced to a limit at which they are most unlikely to cause trouble; at 300° C., $\frac{1}{2}$ hr. is sufficient. These results offer a ready means of eliminating this trouble. A sufficiently high temperature could be attained in a furnace heated by waste heat from an annealing furnace, and the cost of treatment should be quite small.

An explanation is offered of the cause of fire-cracking. At a temperature slightly above 300° C., the incidence of the transformation found usually around 320° C. causes a rapid and marked rise in the internal stress. In the material dealt with in this paper, this never attained the tensile strength; but its near approach to that value indicates that in other material the latter value might be attained when cracking must occur. Anything that would cause local concentration of stress would lead to this result. For instance, the presence of insoluble impurities by setting up such localized stress concentrations would effect this result, and the need for pure alloys is at once explained. Slag or oxide due to poor foundry conditions will obviously act in exactly the same way. As it is shown that starting with a material initially very highly strained the residual stress is, at all temperatures, below that at which it is entirely dissipated, higher than the stress remaining from less severely worked metal, it is easy to

visualize the effect of this in its increased tendency to cause cracking. There can be little doubt that all material will be internally stressed nearly to the breaking point, and anything that is calculated to result in this being more nearly approached is dangerous. Local irregularities of stress due to any cause will add just that small amount of additional stress at the cracking temperature, which will make all the difference between failure and success. A diagrammatic illustration of this hypothesis is shown in Fig. 9.

ACKNOWLEDGMENTS

In conclusion the authors desire to express their thanks to the British Non-Ferrous Metals Research Association for the grants which enabled the work to be undertaken, and also to the Association and the Department of Scientific and Industrial Research for permission to publish the work.

The experimental work was carried out in the Metallurgical Department of Manchester University, and the authors are under a deep obligation to Professor Thompson for the facilities he provided and for his continued interest and helpful criticism throughout the whole of the investigation.

DISCUSSION

WM. B. PRICE, Waterbury, Conn.—This whole phenomena of fire-cracking is simply a question of uneven expansion and contraction and is tied up with the rate of heating or cooling and the amount of reduction prior to the annealing. The magnitude of the stresses is governed by the amount of reduction. A proper correlation of the rolling and annealing schedule will rectify the trouble without special low-temperature annealing to relieve the internal strains. There are zones of compression and non-compression in nickel silver, depending on the amount of reduction, and the rate at which this metal expands or contracts on heating or cooling is governed by these zones. Fire-cracking in the manufacture of sheet metal, tubes, and manufactured articles is the result of insufficient reduction of the metal.

Amorphous Cement and the Formation of Ferrite in the Light of X-ray Evidence

BY FRANCIS B. FOLEY,* CHATTANOOGA, TENN.

(Syracuse Meeting, † October, 1925.)

FROM the point of view of the metallographist, the adaptation of x -rays to the study of the crystal structure of metals is of the greatest importance. While one may hardly consider the findings resulting from x -ray study as revolutionary, their positive nature, compared with the deductions we have been forced to accept from the work that had gone before, gives firmer ground on which to build and furnishes new fields for speculation.

Prior to the advent of the crystallogram, the best work on the crystal structure of steel was that of Osmond and Cartaud.¹ They concluded, from their investigation with percussion figures formed at various temperatures, that alpha, beta, and gamma irons belonged to the cubic system and that they showed well-marked specific characteristics and could not have the same internal structure. What the internal structures were, they had no direct method of determining; but from a consideration of the fact that the 001 plane (that parallel to the cube face) is a plane of perfect cleavage and minimum hardness in alpha iron and that the 111 (octahedral) plane is by far the most important in the crystallography of gamma iron, they were led to suggest the simple cubic arrangement as that of alpha and the face-centered cubic arrangement as that of gamma iron. They suggested the body-centered cubic arrangement as that of beta iron.

The atomic arrangement of the various crystal forms of iron has been quite definitely determined in recent years by means of x -rays and the work of Westgren² and Westgren and Phragmén³ has been rather conclusive. They not only determined the atomic arrangement of alpha, beta, and gamma iron but also that of the high-temperature modification delta.

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¹ F. Osmond and G. Cartaud: Crystallography of Iron, *Jnl. Iron and Steel Inst.* (1906) **71**, 444; also *Trans.* (1906) **37**, 813.

² Westgren: *Jnl. Iron and Steel Inst.* (1921) No. 1, 303.

³ Westgren and Phragmén: *Jnl. Iron and Steel Inst.* (1922).

Alpha iron was found to be body-centered cubic, beta the same as alpha, gamma iron was found to have a face-centered cubic arrangement, and delta body-centered, the same as alpha. The length of the edge of a fundamental cube of delta iron was found to be greater than that of alpha iron but only by an amount that could be accounted for almost exactly by thermal expansion, so that were it possible to preserve alpha iron throughout the temperature range up to the melting point one would find only a gradual increase in the size of the fundamental cube. Of course, the face-centered gamma arrangement intervenes and perhaps the reason for its existence will be found within the atom itself. So we have no simple cubic arrangement of atoms in iron, as was suspected by Osmond and Cartaud, but only two forms—the face-centered and body-centered lattices. Beta iron, as a crystallographic entity, thus ceases to exist.

Austenite has long been considered to be a solution of carbide of iron (Fe_3C) in iron; x-ray results lead us to doubt not only that Fe_3C exists in austenite but that austenite is truly a solid solution. Of course, much depends on the definition of "solid solution." If we accept as requisite to "solid solution" the replacement in the space lattice of an atom of the solvent by a solute atom, austenite is not a solid solution for the carbon atom has been found to occupy a position between corner atoms half way along the edge of the cube, the lattice itself being made up entirely of the metallic atoms, mostly iron of course. This arrangement of the atoms in austenite does not preclude the possibility that there may be a chemical bond between three adjacent iron atoms with a carbon atom, but it is difficult to see where this makes much difference. We know that carbon diffuses quite rapidly in austenite and diffusion is facilitated by the smallness of the atom and by its position in the structure. It is rather difficult to conceive of the diffusion of carbon as a carbide molecule but, on the other hand, it is easy to visualize it as a movement of the atom; and, if chemical bonds hold the carbon to iron atoms, this means the breaking of the chemical bond with one or more iron atoms and the re-establishment of bonds with other iron atoms. As segregation is the result of like atoms grouping locally in a substance, so diffusion is the effort of like atoms to get as far away from one another as possible—one is by an attractive force, the other apparently by a repulsive force. One wonders why the looser packing of atoms in the body-centered cubic alpha iron gives way under the influence of heat to the closer face-centered cubic arrangement of gamma iron, and why this in turn again reverts to the loose body-centered arrangement of delta iron. One wonders also whether cementite is formed again in delta iron as it is in alpha iron.

Long accustomed to speak of cementite as Fe_3C , the x-ray examination of cementite tells us that cementite is orthorhombic, its fundamental unit being comprised of sixteen atoms—twelve iron and four carbon—in other

words of four of the chemist's molecules of Fe_3C . To quote Thomson:⁴ "the term molecule when applied to the solid state is quite ambiguous without further definition." We seem to be on surer ground, for the present at least, in dealing with crystalline matter from the physical point of view.

Figs. 1 and 2 represent, respectively, the lattices of alpha and gamma iron, the dimensions given being those determined by Westgren. In Figs. 3

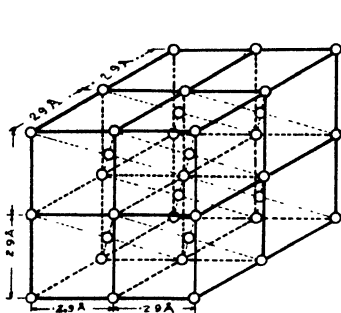


FIG. 1.—SPACE LATTICE OF ALPHA IRON.

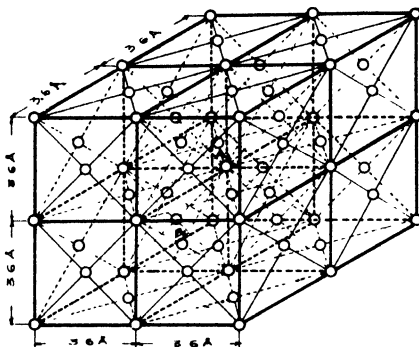


FIG. 2.—SPACE LATTICE OF GAMMA IRON.

and 4, the positions of the atom centers are replaced by spheres representing the atoms so that in Fig. 3 (alpha) the body-center atom touches all eight corner atoms and in Fig. 4 (gamma) the face-center atoms touch the four corner atoms. It is only with reference to a single fundamental cube that one may designate certain atoms as corner, body-center, or face-

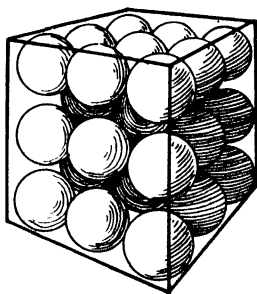


FIG. 3.—BODY-CENTERED CUBIC PACKING, ALPHA IRON.

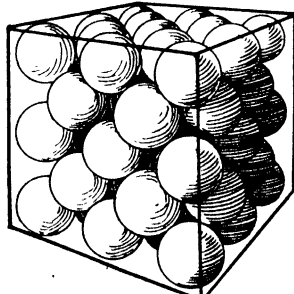


FIG. 4.—FACE-CENTERED CUBIC PACKING, GAMMA IRON.

center atoms—their identity is lost in the crystal aggregate. The sphere is used as a convenience only in illustrating the atom; actually the atom is, as Doctor Aston⁵ puts it, as empty as the solar system, its constituent

⁴ Sir J. J. Thomson: *The Electron in Chemistry*, The Franklin Institute, 1923.

⁵ *Nature*, Nov. 25, 1922.

charges, protons and electrons, filling not the million millionth part of its volume.

How does one fit the ideas built up in the past from insufficient data to the results obtained with this new tool? Take, for example, the formation of austenite from liquid steel. A portion of the equilibrium diagram of the carbon-iron system (delta iron is omitted for convenience) is shown in Fig. 5. The freezing of a steel of C per cent. carbon has commonly been described substantially as follows: The freezing is selective, starting at temperature t' by the formation of crystal nuclei of relatively pure iron (carbon C' per cent.). As the temperature falls, crystals of higher carbon content form and attach themselves to the growing nuclei until, at temperature t'' , the solid crystals have an average carbon content of C'' per cent., and with further drop in temperature to t''' the addition of crystals of still higher carbon have increased the carbon in the solid crystals

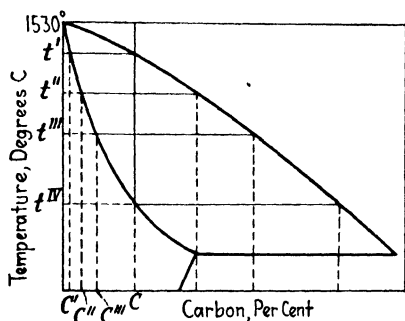


FIG. 5.—PORTION OF FE-C EQUILIBRIUM DIAGRAM.

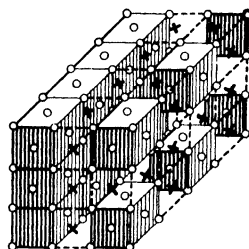


FIG. 6.—CRYSTAL FORMATION BY BLOCKS.

to C''' per cent. and so forth, the process ending with the complete solidification at temperature t^IV with the crystalline mass averaging C per cent. of carbon. This process has been illustrated by means of cubes.⁶ As a result of this block method of illustration, an amorphous intercrystalline cement has been postulated as existing between the individual crystals. Without sufficient room in which to form a cube, certain liquid atoms are said to be unable to adjust themselves in accordance with the crystal pattern and therefore fail to crystallize, remaining amorphous. To the left, in Fig. 6, is a crystal face made up of twelve fundamental face-centered cubes (they might, as well, be body-centered for our present purpose). The circles represent atom centers—the units are represented as blocks for the sake of clearness in illustration. The blocks to the right represent crystal units, which we will imagine as being in position to attach themselves to the crystal face. If they make contact with the crystal face what will happen? The corner and face-center atoms of the units become superimposed on the corresponding atoms of the crystal face! The only

⁶ Rosenhain: Introduction to Physical Metallurgy, Fig. 14, Plate IV (1919).

way we can attach these units to the crystal face is by bringing atoms in to the positions indicated by x and having the units take up a position, as shown, one cube distance from the crystal face. By such a process we should have crystal growth taking place atom by atom and at the same time cube by cube. If it is necessary to have this happen partly atom by atom, and it cannot progress cube by cube, why consider the cube at all except as the nucleus?

What happens to amorphous intercrystalline cement when crystals are built up atom by atom instead of a cube at a time? Two dimensions

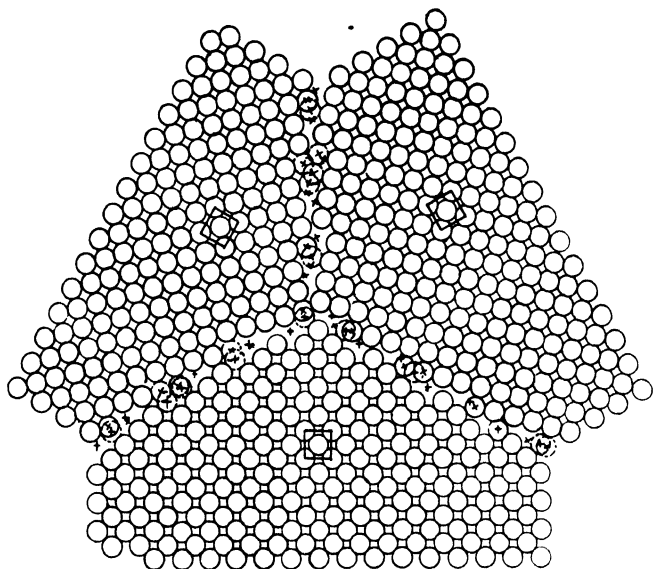


FIG. 7.

are all that can be clearly shown in two dimensional pages and three crystals have been so constructed in Fig. 7. The three crystals were started at random points and directed so as to join at boundaries set at 120° apart; the arrangement is face-centered, as in austenite. When the crystal boundaries are reached, a space may be found that will accommodate an atom but crystal centers of two adjacent crystals may happen in that space. Of course if there is room for an atom, there is one there somewhere—it becomes a matter of placing it. Where one position seemed more stable than the other, where it could touch two other atoms in one crystal rather than only one atom in the other, a solid atom is drawn about the center and the alternative position is shown dotted. Where there seemed no choice, both positions are shown by a dotted atom.

Sometimes two atoms are to be placed in three alternative positions; then the same scheme is applied. Some voids are left where no atom may fit; whether such voids exist or not is a question. Perhaps such spaces are filled by a slight spreading of the atoms adjacent to the boundaries, which would lead to a slight disregistry of the atoms in the neighborhood. This is all we can see of an amorphous intercrystalline cement. But why is it necessary to postulate or account for such amorphous material?

It has been shown that when metals are parted at low temperature, the path of rupture is transcrystalline; and that when it is parted at elevated temperatures, the rupture is intercrystalline. To explain this amorphous cement has been invented. It is said that amorphous materials generally are hard and unyielding like glass, when cold, but become plastic and flow readily when hot. Therefore an amorphous cement between crystals would be unyielding at low temperatures and fracture would occur through the body of the crystals; but at elevated temperatures, the amorphous cement would become weaker than the body of the crystals and the path of rupture would follow the crystal boundaries. Then we have the block system of crystal formation and growth to account for the cement, necessity being the mother of invention. Was there any necessity?

There are no fixed crystal boundaries at elevated temperatures. Under the influence of temperature, crystals grow; as shown, this growth is an atom by atom procedure. One crystal robs another, its neighbor, and it becomes a survival of the fittest. The little fellows are probably wiped out quickly and, in time, it becomes a battle of giants. One can readily conceive of the crystal boundaries as being the weakest point in the structure and the point to fail when stress is applied. At the moment of stress application, there are atoms at the grain boundaries loosely held by adjacent crystals, having parted company with one and not yet settled in the lattice of the one to which they have been drawn. Conceivably such loosely held atoms may fly off into the air when hot metal is ruptured.

The *x*-ray seems to show that no amorphous films are formed by cold working the surface of cold metals; slip interference satisfactorily explains the raising of the elastic limit by cold working (heretofore explained by the production of amorphous films at planes of slip) and amorphous metal is not essential to the explanation of intercrystalline weakness at high temperatures. The amorphous theory, as concerns metals, seems weak at all temperatures.

THE FORMATION OF FREE FERRITE

It is interesting to consider the formation of free ferrite in the light of our present knowledge. It, of course, forms only in hypo-eutectoid steels. We know that, as a general rule, free ferrite forms an envelope about

masses of pearlite and gives a network appearance in a plane section. No doubt the ferrite envelope occupies the position of the grain boundaries that existed in austenite from which the pearlite-ferrite aggregate formed. Many of us have thought of the free ferrite as a constituent that is rejected by the austenite to its grain boundaries at a proper temperature during cooling (the A_{r3}). Nowadays we visualize something of the sort of thing shown in Fig. 3 as ferrite, or alpha iron, and find it rather difficult to imagine such aggregations of atoms as being rejected from a crystal structure, such as that of gamma iron (Fig. 4)—we are hardly able to conceive of such aggregations as migrating through another lattice arrangement. The more rational explanation of the formation of a constituent such as ferrite is based on a movement of single atoms.

The change from gamma to alpha iron is allotropic and much hinges on the definition of allotropy. If one holds to the rejection idea, in which alpha iron forms in austenite and is then rejected as a foreign body to the exterior of the crystal, it practically amounts to saying that the atom itself undergoes allotropic change because it is almost inconceivable that one crystalline arrangement is passing through another in such a process. The word "almost" is used advisedly, for we are aware of the mixed orientation that exists in interpenetrating twins. The best criterion of allotropy is, doubtlessly, the change of crystal form; and it is on this basis that most metallographists have discarded beta as an allotropic form of iron—not, to be sure, on this basis alone, but this is perhaps the point on which it has in most cases been rejected. The atom certainly changes its crystal habit when passing from gamma to alpha, and it seems reasonable to believe that something happens within the atom to cause this change. We also believe a change takes place within the atom when iron passes from the magnetic to the non-magnetic state and the existence of isotopes has been demonstrated. But these last are undoubtedly of a different character than that which produces a different crystal habit and which we designate as allotropic. But allowing that allotropy resides within the atom and that it is not necessary that atoms be grouped in a body-centered arrangement in order to be designated as the alpha form, so that a lone atom may transform, it hardly seems likely that atoms born in the center of a gamma crystal would be forced to the exterior of the crystal before meeting with others of their kind to form crystal units of alpha iron. However, alpha iron is usually (not always) found occupying the position of the boundaries of old austenite crystals, and our argument is that ferrite is not formed within the crystals and rejected to the grain boundaries but forms at the exterior of austenite crystals.

Other things being equal, particularly as regards carbon distribution, the grain or crystal boundary is the place where recrystallization would be most apt to start. First of all, the atoms at crystal boundaries are freer to assume a new orientation because such atoms, as pointed out ear-

lier in this paper, are continually engaged in the process of adopting new orientation incident to crystal growth and may, as well, set up the new crystal structure that is their habit under the temperature conditions prevailing. A second reason may be found in a consideration of the available energy at the surface and that within the body of a crystal. This will be made clear by reference to Fig. 2. A corner atom within a crystal, such as *A*, touches twelve other atoms and its energy is disseminated in eight adjoining cubes. Every atom within the crystal is situated in the same manner. Fig. 2 is a conventional drawing and *B* is shown as a face-center atom but, leaving out the dotted and solid lines, its relative position is not different than that of *A*. At the crystal face, however, there is a difference. An atom on the face of a crystal, such as Fig. 2, is touching but eight other atoms and has its energy disseminated within four units. It appears to have available energy in excess of that necessary for it to hold its position in the lattice; this energy is available for the start of recrystallization.

We know that ferrite (alpha iron) does not always occupy the position of the grain boundaries of the austenite. In cast low-carbon steels we have seen a network of pearlite enclosing ferrite areas. Again, in the case of Widmanstätten structure, ferrite is found in what were the 111, or octahedral planes of the austenite. Both these cases may be explained, at least in part, by the predominance of iron atoms at the nuclei of recrystallization. According to Westgren, the carbon atom occupies a position between corner atoms along the cube edge. Thus any plane parallel to the cube face (001) contains carbon atoms. None will be found in the octahedral plane, which will be made up entirely of metal atoms. This seems an interesting observation in connection with the formation of Widmanstätten structure.

In the case of the formation of ferrite at the crystal boundaries of austenite, it is easy to visualize the atoms that have been taking part in the process of grain growth as forming the nuclei of the new allotrope—alpha. In the new lattice, there is no room for the carbon atom, which must find its way into the untransformed gamma lattice. The gamma lattice is progressively broken down to add atoms to the alpha nuclei and thus the carbon atoms are thrust toward the center of the crystal.

DISCUSSION

E. E. THUM, New York, N. Y.—The structures shown in Fig. 7 can be readily made in the kitchen. Place a dishpan containing a couple of inches of water, a piece of ivory soap, and a dish mop (one that has a wooden handle, and a tuft of cotton thread at the end of a piece of twisted wire) over a gas jet. Then as the water heats, a stream of fine bubbles, apparently exactly the same in size, will rise to the surface from the point

where the twisted steel enters the wooden handle. These bubbles collect in blocks, perfectly arranged in a geometric pattern, and float around, finally attaching themselves to the edges of the pan or the floating wood. You will get a typical arrangement, such as is shown in Fig. 7, with the intercrystalline cavities shown here; but there is no suggestion of amorphous cement in such a bubble aggregate, that is to say, the geometric arrangement is apparently perfect even out to the intersection. You can shove these bubble groups around with a knife and see the development of slip planes, and you can get a close picture of many ideas that have been introduced into the literature of *x*-ray investigation and theoretical metallurgy. One thing to remember is that bubbles of this sort are different from atoms, they have only a slight gravitational force acting from a distance; if this were not so they would not aggregate themselves into one orderly mass.

The Current Theories of the Hardening of Steel Thirty Years Later

ALBERT SAUVEUR*

(New York Meeting, February, 1926)

MY FIRST paper dealing with the theories of the hardening of steel by rapid cooling was published in the *Transactions* of this Institute in 1896—30 years ago—under the title “The Microstructure of Steel and the Current Theories of Hardening,” hence, also, the title of the present paper. It was extensively discussed and was, I believe, one of the starting points of many subsequent papers and discussions of the same subject, discussions which at times became almost violent and which led to the formation of different schools such as the “Carbonists” and the “Allotropists.” Some of the older members of the Institute, who took part in the debate or who were interested observers, will, I am sure, have kept a vivid remembrance of it. The controversy gradually quieted down, apparently for lack of ammunition, without any side acknowledging defeat. Recently, however, interest in it has been revived through the claims of some that these vexed questions had at last been solved.

In an effort to ascertain if possible the prevailing view of those best qualified to express an opinion a questionnaire was submitted to the following gentlemen:

J. O. Arnold
Edgar C. Bain
Carl Benedicks
N. Belaiew
H. M. Boylston
Harry Brearley
G. K. Burgess
William Campbell
H. C. H. Carpenter
Pierre Chevenard
P. Dejean
C. A. Edwards
F. Giolliti
G. Grenet
Leon Guillet

Sir Robert Hadfield
W. H. Hatfield
Samuel L. Hoyt
Kôtarô Honda
Zay Jeffries
H. Le Chatelier
H. H. Lester
Francis F. Lucas
John A. Mathews
A. McCance
Albert Portevin
Walter Rosenhain
Bradley Stoughton
F. C. Thompson

* Gordon McKay Professor of Metallurgy and Metallography in Harvard University.

The questions asked were:

1. What in your opinion is the nature of martensite and what causes its hardness?

2. What are the conditions necessary for its formation, and the mechanism of that formation?

3. If you believe it to be a solid solution of iron and carbon, or of iron and the carbide Fe_3C , what position do you think the carbon atoms or the carbide molecules occupy in the space lattices of the crystals?

4. What part, if any, do you think that strains play in the hardening of steel?

It is very gratifying to be able to report that 23¹ of the 29 eminent metallurgists consulted were good enough to reply, and I desire to place on record my sincere appreciation of their invaluable cooperation. The answers received from these gentlemen will be found in full in an appendix to this paper. They constitute an important symposium of the Hardening Theories.

Armed with the up-to-date information these answers brought me, I propose to discuss briefly and as impartially and as clearly as I can, the phenomenon of the Hardening of Steel.

AUSTENITE

Since the hardening of steel is obviously due to a transformation of austenite into the condition existing in hardened steel, it seems advisable at the outset to recall the nature of that constituent. While austenite is quite universally believed to be a solid solution in which the iron is in the allotropic condition known as gamma, opinions differ as to the condition of the carbon dissolved in this gamma iron, some believing that the carbon is present in atomic dispersion, others that it exists as the carbide Fe_3C or cementite. From the answers received in regard to the condition of the carbon in martensite considered as a solid solution, soon to be discussed, it is, I believe, warranted to conclude that a greater number of those consulted believe that carbon in austenite is present as carbide compared to the number of those who believe that it is present in atomic dispersion.

It is evident, however, that at the very outset of our inquiry we face a decided difference of opinion on a rather vital point, and that we must proceed by assuming that austenite is a solid solution of *carbon* or of the *carbide* Fe_3C in gamma iron.

MARTENSITE

The constituent found in hardened steel and to which it is believed the hardness of the steel is due has been called martensite. It generally

¹ Chevenard and Portevin sent a joint reply.

occurs in the form of fine needles. Obviously those martensitic needles result from the transformation of austenite under certain conditions soon to be considered.

A sharp distinction should be made, however, between hardened (martensitic) steel and martensite because the former never consists exclusively of martensite. Hardened steel is an aggregate. It does necessarily contain martensite, and it is possible that it owes its hardness chiefly, if not wholly, to its presence, but it also contains one at least of the following constituents: undecomposed austenite, troostite, cementite or ferrite. I am not aware that the x-ray spectrum of martensitic steel has ever failed to reveal the presence of gamma lines, that is, of austenite, while cementite lines very frequently occur. From the contention that martensite is a solid solution, hence a homogeneous phase, it would not follow, therefore, that hardened (martensitic) steel is a solid solution.

On the reasonable assumption that hardened steel owes a great part of its hardness at least to the presence of martensite, let us examine the evidences we have throwing light upon the nature of martensite and the conditions necessary for its formation.

Since martensite is obviously an alloy of iron and carbon we are naturally concerned with (1) the condition of the iron present in martensite; (2) the condition of the carbon present in martensite; and (3) the nature of the bond uniting the iron and the carbon. These are fundamental considerations and we shall not be able to proceed very far unless the questions involved can be satisfactorily answered.

CONDITION OF IRON IN MARTENSITE

We know that iron may exist in two at least, and some believe in three, allotropic forms; namely, gamma, beta, and alpha iron. I intentionally disregard the possible existence at a very high temperature of a fourth variety, delta iron, in steels containing less than 0.38 per cent. carbon, as I do not believe that anyone has ever claimed that delta iron was present in martensite.

Assuming, then, the possible existence at room temperature of three allotropic forms of iron, there are seven mathematical possibilities in regard to the condition of iron in martensite as follows:

1. Gamma iron
2. Beta iron
3. Alpha iron
4. Partly gamma and partly beta
5. Partly gamma and partly alpha
6. Partly beta and partly alpha
7. Partly gamma, partly beta, and partly alpha.

HONDA.—“Martensite is a solid solution of carbon in alpha iron, or atomically expressed, it has a body-centered cubic lattice, as in ferrite, but with carbon atoms in the interspace of the lattice.”

BAIN.—“Mechanically, freshly formed martensite may resemble a true solid solution of carbon in alpha iron . . . ”

McCANCE.—“Martensite in my opinion is an enforced solution of carbon in a mixture of iron and gamma iron . . . ” Also, “I believe that the carbon atoms exist at the center of unit cubes . . . ”

The claim that molecules of the carbide Fe_3C cannot be present in solution in gamma or alpha iron for lack of room to accommodate them between the iron atoms in the space lattices, while difficult of refutation, fails to carry conviction. Some of us feel that our knowledge of these space lattices and of the constitution of matter in general is not sufficiently intimate to warrant any such dogmatic statement. Lester at least conceives the possibility of placing these molecules of carbide in the space lattices (see Lester's reply).

Campbell refers to the presence of both carbon and carbide in martensite.

CAMPBELL.—“Martensite is ferrite or perhaps alpha iron, with a small amount of carbon in solid solution and containing iron carbide in a very fine state of dispersion . . . ”

Sir Robert Hadfield, Mathews, and Stoughton admit that they do not know.

SIR ROBERT HADFIELD.—“Martensite (martensitic structure) is believed to be a solid solution of carbon or of carbide in alpha iron. Sufficient evidence does not seem to have been accumulated that would enable anyone to determine definitely . . . whether the carbon, when in solid solution exists as atoms of carbon or molecules of Fe_3C .”

MATHEWS.—“I consider martensite as a solid solution, but whether of carbon or carbide I am not yet certain . . . ”

STOUGHTON.—“ . . . have used the general term of iron with carbon, without intending to indicate thereby any prejudice against a belief in a solid solution of iron with cementite.”

From the answers received from Belaiew, Chevenard, Guillet, Hoyt, and Portevin, the view favored by these gentlemen in regard to the condition of the carbon in martensite is not clear.

Summing up, it is apparent that a substantial majority of those consulted are inclined to believe that carbon is present in martensite in the form of the carbide Fe_3C , and that it is justifiable to conclude that it is the prevailing view.

BOND UNITING IRON AND CARBON

The third fundamental consideration deals with the nature of the bond uniting iron and carbon in martensite.

Martensite must of necessity be (1) a definite chemical compound, (2) a colloidal solution, (3) a solid solution, or (4) an aggregate.

One metallurgist, Arnold, has claimed that martensite was a definite chemical compound, namely, the carbide Fe_{24}C . He has had few followers and his hypothesis is generally held untenable. One at least of the gentlemen consulted, namely, Grenet, considers the possibility of martensite being a colloidal solution when he writes:

"This extreme fineness at which structural equilibrium ceases to be distinguishable from physico-chemical equilibrium characterizes, in my opinion, the colloidal state. And the term colloidal aggregate is better suited, I believe, to the aggregates designated as martensite than to the aggregates called troostite and sorbite."

The nature of martensite is thus described by those consulted.

BAIN.—"Martensite is the product—under certain specific conditions—of the allotropic change undergone by solid solutions of gamma iron."

BENEDICKS.—"Martensite is a solid solution of carbon ('free' or 'combined') in alpha iron."

BELAIEW.—"Martensite is the hard constituent of quenched iron carbon alloys."

BOYLSTON.—"In my opinion, martensite is a mixture of a solid solution of iron carbide in beta iron and some alpha iron probably in the form of troostite."

BREARLEY.—"Martensite is carbide dissolved or finely dispersed in alpha iron."

CAMPBELL.—"Martensite is ferrite or perhaps alpha iron with a small amount of carbon in solid solution, and containing iron carbide in a very fine state of dispersion . . ."

CHEVENARD AND PORTEVIN.—"Martensite is a solid solution in which iron is in the alpha condition . . ."

DEJEAN.—" . . . it is logical to infer that martensite is a solid solution of carbide in alpha iron."

GRENET.—"As I do not know the exact definition of martensite I do not know the characteristics by which it can be defined."

GUILLET.—"Martensite appears to be alpha iron and gamma iron holding carbon in solution."

SIR ROBERT HADFIELD.—"Martensite (martensitic structure) is believed to be a solid solution of carbon or of carbide of iron in alpha iron."

HOYT.—“My opinion of the nature of martensite is practically as given in the Hanemann-Schrader paper of 1925.”

HATFIELD.—“ . . . largely a solid solution.”

HONDA.—“Martensite is a solid solution of carbon in alpha iron . . . ”

JEFFRIES.—“I believe that freshly formed martensite in carbon containing steel is fine grained ferrite, crystallizing with a body-centered space lattice, in which the carbon is largely atomically dispersed . . . ”

LE CHATELIER.—Professor Le Chatelier undoubtedly regards martensite as a solid solution of the carbide Fe_3C in alpha iron.

LESTER.—“It seems to me that martensite may be defined as an aggregate of small distorted iron crystals, which crystals may represent a solid solution of iron and carbon; the crystals are usually those of alpha iron, but gamma iron crystals may be present and may even preponderate in rare cases.”

LUCAS.—“In my opinion martensite is a decomposition of austenite along the octahedral crystallographic planes in the form of iron and iron-carbide. That martensite is not a solid solution seems to be true because more than one constituent is visible under high magnification. The conclusion seems justified that iron-carbide must be present in martensite and it is my opinion that the iron is probably present in the alpha state. The carbide must be present in a highly dispersed condition.”

MATHEWS.—“I consider martensite as a solid solution but whether of carbon or carbide I am not yet certain.”

MCCANCE.—“Martensite, in my opinion, is an enforced solution of carbon in a mixture of alpha iron and gamma iron, but in which the alpha iron is largely predominating.”

STOUGHTON.—“I believe that martensite is the first stage in the decomposition of austenite, and that the bulk of the evidence indicates that it is the beginning of a decomposition of the solid solution of carbon and gamma iron.”

THOMPSON.—“Martensite is a supersaturated solid solution of carbon and iron carbide in alpha iron, together with, under normal conditions, a certain amount, probably small, of unchanged austenite.”

While from these answers it would seem as if it is quite generally held that martensite is a solid solution, it should be noted that many refer to the presence of gamma iron (undecomposed austenite?) and, at least in aged martensite, of cementite, which as a matter of fact would convert it into an aggregate. Lucas unhesitatingly states that martensite is an aggregate, and indeed, following Jeffries and others, we should regard martensite as made up of submicroscopic grains of ferrite with

dispersed particles of cementite. Whether the alpha ferrite contains or not some carbon in solution appears to them to be relatively immaterial.

FORMATION OF MARTENSITE

Passing now to the conditions necessary to form martensite it is evident from the answers received that metallurgists agree that in order to produce it and to retain it at room temperature, in iron-carbon alloys, the allotropic transformation of gamma iron must be delayed by sufficiently rapid cooling until a temperature of some 300° C. is reached. In the presence of elements such as nickel and manganese, sometimes referred to as retarding elements, less rapid cooling suffices. Indeed, slow cooling in air or even in the furnace of such alloy steels may cause the allotropic change to take place at 300° C. and the steel to become martensitic. It is generally held that when austenite transforms at such low temperatures, the gamma to alpha allotropic transformation takes place, but for lack of the necessary plasticity the carbon or the carbide of iron is retained in solution in alpha iron although the latter has little if any dissolving power for carbon. This solid solution of carbon in alpha iron, therefore, is necessarily supersaturated, which, according to some, may account in part at least for its great hardness.

WHY MARTENSITE IS HARD

Whether a solid solution or an aggregate, we must seek the cause of the intense hardness of martensite. The following reasons have been given:

1. Because of the hardness of the carbon it contains;
2. Because of the hardness of the carbide it contains;
3. Because of the hardness of the iron it contains;
4. Because it is a solid solution;
5. Because it is a supersaturated solid solution;
6. Because of the distortion of the crystal lattices;
7. Because of the extreme fineness of its grains;
8. Because of the presence of numerous minute particles of the carbide Fe_3C , and
9. Because of internal strains.

If we turn to those who have been consulted, we shall find that there is decided lack of agreement on this very important point.

BAIN.—“Martensite is hard because of the tremendous slip obstructions of both the small or badly crystallized alpha iron grains, and the tiny carbide particles subsequently developed.”

BENEDICKS.—“ . . . its hardness is due to the disturbance of the alpha lattice caused by the solute having a low natural miscibility with alpha iron.”

BELAIEW.—“ . . . the whole potential amount of deformation inherent in any and every martensitic grain has been exhausted—whence its hardness.”

CAMPBELL.—“Martensite is . . . containing iron carbide in a very fine state of dispersion, and the iron carbide is the cause of hardness due to slip interference.”

CHEVENARD AND PORTEVIN.—“One might as well ask why diamond is much harder than graphite . . . ”

DEJEAN.—“In regard to the hardness of martensite, it is probably closely related with its method of formation at a low temperature.”

GUILLET.—“The extremely small size of the constituents explains the hardness.”

SIR ROBERT HADFIELD.—“Sufficient evidence does not seem to have been accumulated that would enable anyone to determine definitely what is the cause of the hardness of martensite.”

HATFIELD.—“It would appear that the cause of its hardness is due to the fact that it is essentially, though not completely, a solid solution.”

HOYT.—“The hardness is due to the phase of about 0.9 per cent. carbon in which the carbon and iron are in forced solution or combination. The high mineralogical hardness would be due to new interatomic bonds which are thereby set up.”

HONDA.—“According to my view, at least two-thirds of the great hardness of martensite (650 in Brinell Scale) is due to the effect of the hardening carbon as explained above, that is, carbon atoms present in the interspace of the lattice.”

JEFFRIES.—“ . . . the hardness is due principally to the grain refinement but partly to the carbon.”

LE CHATELIER.—“I do not know of any previous observation by which this hardness can be explained.”

LESTER.—“The hardness of martensite seems to me to be due to the combined effects of small crystal size and warped crystal planes in preventing slip along atomic planes.”

LUCAS.—“In my opinion, the hardness of martensite is due to the presence of iron carbide in a highly dispersed condition.”

MCCANCE.—“The normal alpha iron space lattice is consequently distorted, owing to the presence of the carbon atom, and the hardness of martensite is a consequence of this state of distortion.”

STOUGHTON.—“I believe that its hardness is caused by internal stresses within the crystal which prevent intracrystalline slippage.”

THOMPSON.—“The hardness is due to several factors. In the first place, the needles formed act as strengthening scaffolds throughout the mass. Secondly, there must be an appreciable amount of distortion of the space lattices which will also increase the hardness, and finally I do not see how there can be but severe internal stresses which also have the same effect.”

If it be attempted to analyze these views in regard to the cause of the hardness of martensite, I think it will be found that Guillet and Jeffries attribute the hardness chiefly to the smallness of the grains, Benedicks, Honda and McCance chiefly to lattice distortions, Bain and Lester to both smallness of grain and lattice distortion, Thompson to lattice distortion and strains, Campbell and Lucas to the presence of carbide particles, Hatfield to the state of solution and Stoughton to internal stresses within the crystal.

POSITIONS OCCUPIED BY CARBON ATOMS OR CARBIDE MOLECULES

Assuming with most, martensite, when freshly formed at least, to be a solid solution of carbon or of the carbide Fe_3C in alpha iron, let us inquire into the positions occupied by the carbon atoms or by the carbide molecules in the space lattices of the alpha crystals. A few only have had the courage to answer that question.

BAIN.—“It is not known just where the carbon atoms are located in reference to alpha iron space lattice, but the evidence points strongly to interstitial spaces and not the customary lattice points usually occupied by solute atoms.”

BELAIEW.—“According to the latest x-ray evidence, the carbon atoms occupy the central points of the cubes in the face-centered lattice of the gamma iron. Such structure corresponds to what has been called a solid solution of carbon in iron or austenite.”

HATFIELD.—“It might be reasonable to assume that the iron atoms of the carbide aggregate tend to take up positions in the normal space lattice of the iron, the carbon atoms being probably situated inside the normal space lattice of the iron atoms.”

HONDA.—“The carbon atoms are in the interspace of the lattice.”

HOYT.—“After calculating the number of atoms of carbon which may replace the iron atoms in the body-centered cubic lattice, and give the

density and lattice parameter, as measured, my opinion is that a 0.9 per cent. carbon martensite has about half its carbon atoms in the lattice and the other half of its carbon atoms in the interstices. No cause for such an atomic arrangement is known to me and it may be found later, contrary to this picture, that the distribution is simple."

JEFFRIES.—"I believe that such carbon as remains in atomic dispersion in the ferrite is probably in between the space lattice points."

LESTER.—"I think that the carbon atoms occupy positions near to, but not necessarily on, lattice points of the alpha iron crystals. It seems probable that each carbon atom may be associated with three adjacent iron atoms, the four atoms occupying positions near to, but not on lattice points and forming in effect a molecule of iron carbide. From this view, we obtain that the solution is a molecular dispersion of iron carbide in alpha iron, this solution differs but little from an atomic solution of carbon in alpha iron."

MCCANCE.—"I believe that the carbon atoms exist at the center of unit cubes of eight iron atoms and replace the center iron atom in the normal alpha iron lattice."

It is evident, therefore, that there is no substantial agreement among those who have devoted much time to the *x*-ray analysis of steel as to the position occupied by the carbon in the crystal lattice of alpha iron.

INFLUENCE OF STRAINS

My last question referred to the part played by strains in the hardening of steel. Here again opinions differ widely, some holding that strains play a very important part, some no part at all, while others believe that they may to a notable extent contribute to the hardness.

BAIN.—"Strains play a vital part in the hardening of steel in so far as the pieces crack and break in the quench or subsequently; otherwise, except for a possible action to decrease the amount of residual austenite in proportion to their severity, they probably have nothing to do with the hardening. They are an effect, not a cause."

BENEDICKS.—"The hardening of steel being due to forcing a less soluble substance to remain in solution, it is necessarily accompanied by strains in the crystal lattice; on the contrary, the earlier debated strains, due to the difference in cooling speed between the inner and outer parts of a quenched specimen, have no essential influence on hardening."

BELAIEW.—"I believe internal strains play an important part in the *hardening* of steel chiefly because of the volume changes accompanying the transformations; *i.e.*, strains determine in part to what extent the main transformation takes place. I do not believe that internal strains

have any important direct bearing on the *hardness* of steel. If there is any effect, internal strains would probably decrease rather than increase hardness."

BREARLEY.—"Stresses and strains are important causes of hardening but I cannot make any quantitative estimates of their influence."

CAMPBELL.—"I do not think that strains play any material part in the hardening of steel."

DEJEAN.—"It cannot be denied that cold working and quenching impart to steels often very similar properties. It is also probable that the formation of martensite which takes place at a low temperature accompanied by an important change of volume, produces in the steel tensions of an order comparable to those resulting from cold working. One should avoid, however, carrying too far the resemblance between these two phenomena."

GUILLET.—"Strains play a very small part in quenching."

SIR ROBERT HADFIELD.—"Cases are well known in which stress alone, resulting in strain, but without alteration of lattice, is sufficient to produce a considerable increase in the ball hardness of certain steels. On the other hand, it has not been conclusively determined whether the presence of strain is always a necessary condition of the hardening."

HATFIELD.—"I have already said that I think that the internal stress, and probably also permanent strain effects resulting from quenching, if tempered at a low temperature, *i.e.*, a temperature below that at which, so far as we know, the constitution can be modified, the hardness becomes less and the ductility greatly increased."

HOYT.—"Due to the fact that hardening involves an appreciable volume change, I believe that strains must play an important role in the process through the pressure effects which they will set up. If the pressure distribution were known, the effect would be that predicted by applying the principle of Le Chatelier."

JEFFRIES.—"I believe internal strains play an important part in the *hardening* of steel chiefly because of volume changes accompanying the transformation; *i.e.*, strains determine in part to what extent the main transformation takes place. I do not believe that internal strains have any important direct bearing on the *hardness* of steel. If there is any effect, internal strains would probably decrease rather than increase hardness."

LE CHATELIER.—"I do not believe that strains can play any role in the hardening of steel. When the stresses are uniformly applied to a

metal in such a way as to prevent any deformation, no increase of hardness results, as this depends solely upon the extent of the deformations. Since the stresses which may occur when gamma iron changes to alpha are not accompanied by deformation, they cannot be a cause of hardness."

LESTER.—"If strains be taken as displacements of atoms from positions of stability then strains within the crystals may be regarded as one of the two principal factors in the hardening of steel, the other being the smallness of the crystals. In this the strains measure the distortion within the crystals; the distortion and not the strain may be regarded as the primary cause of the hardness."

LUCAS.—"Practically an unimportant one—Strains, in my opinion, are an effect of hardening rather than a cause."

MATHEWS.—" . . . it seems to me that in addition to Jeffries' theory, stress does play some part, but not a prominent part."

MCCANCE.—"Strains take no part in the hardening of steel."

STOUGHTON.—"I believe that strains existing in the interatomic bonds within the space lattices are chiefly responsible for the inflexibility which I associate with the hardness of steel. I believe that the bonds are under such stress that they have not the elasticity to permit deformation without rupture. The slip interference theory for the hardness of overstrained metals seems to meet that particular type of hardness only to a limited extent."

THOMPSON.—"Hardening cracks are the best evidence for the existence of very severe internal stresses approximating to the tensile strength of the material."

CONCLUSIONS

After this brief survey of the views held by those who have devoted much time to the study of the phenomenon of the hardening of steel, I believe that it is not possible to tell what is the prevailing view of metallurgists. Differences of opinion are met with at every stage, in regard to the condition of the carbon dissolved in gamma and in alpha iron, to the position occupied by the carbon atoms or by the carbide molecules in the crystal structure, to the nature of martensite and especially to its hardness, which is attributed to many causes.

It is evident that those who believe they have solved the problem of the hardening of steel have done so only to their own satisfaction and to that of a few followers. The best that can be done is to state that it is generally, but not by any means universally, held (1) that freshly formed martensite is a solid solution of carbon or of the carbide Fe_3C in alpha iron; (2) that martensite forms, and is retained, when austenite transforms in

the vicinity of 300° C.; (3) that on aging, minute particles of the carbide are thrown out of solution, converting the martensite into an aggregate; (4) that the hardness of martensite is due wholly or partly to one or more of the following causes:

(1) To its being a solid solution; (2) a supersaturated solid solution; (3) to the fineness of its grains; (4) to distorted space lattices; (5) to the presence of minute particles of the carbide, and (6) to internal strains.

As to the positions of the carbon or carbide in the crystal lattices, the least said the better.

It is also generally held that troostite is a very fine aggregate of ferrite and cementite.

It should be noted that, accepting these views of the nature of martensite and troostite, hardened steel frequently contains (1) undecomposed austenite which is one phase; (2) martensite, another phase, and (3) troostite, a mixture of two phases, ferrite and cementite, that is, in all, four phases, which is not permissible in a system of two components. There must be something wrong with this conception.

Comparing the situation today with that of 30 years ago as presented in my first paper, the only progress (?) made towards a solution of the problem may, I believe, be thus summarized: (1) Abandonment of the belief in the existence of beta iron; (2) *x*-ray analysis of iron-carbon alloys by which it is shown that gamma iron has a face-centered space lattice and alpha iron as well as the iron present in martensite, a body-centered space lattice, and (3) the belief expressed by some that the hardness of martensite might be caused primarily (a) by the presence of extremely small (submicroscopic) ferrite grains or (b) by the distortion of the space lattices resulting from the presence of carbon atoms in enforced solid solution. This does not constitute a very material advance, if advance at all, seeing that it has also introduced additional controversial matter.

ANSWER OF THE AUTHOR TO THE QUESTIONNAIRE

In answering my questionnaire and in briefly expressing my views in regard to the hardening of steel, I do not claim in any way to have solved the problem discussed in this paper. I feel today exactly as I did 30 years ago, when, after outlining some conception of the possible cause of hardening, I wrote, in concluding my paper: "The writer does not wish to advance here any new theory. Indeed, if he knew that his remarks would be so interpreted he would refrain from giving them shape. He only feels that they may contain some element of truth which may help in solving the problem discussed in this paper, and if his arguments and deductions are not sound, he hopes they will be promptly refuted."

Fortunately, I am not wedded to any theory. I am ready to abandon any I may at one time have defended for any other which may appear

more logical or more useful. Theories are tools, and we should use the best tools obtainable.

While referring to my early contribution, it may not be without interest to reproduce here some of my arguments as they seem to have anticipated the recent claims that the hardness of martensite is due primarily to the smallness of the ferrite grains and to the presence of minute cementite particles, although perhaps rather clumsily expressed at the time.

The hardness of martensite can very well be attributed, then, to the diffusion through its mass of the carbide Fe_3C , which we *know* exists in steel below the critical range, and which we *know* to be extremely hard. It will no doubt be argued that if the hardness of martensite is produced by the presence of a certain amount of Fe_3C , or cementite, then the pearlite of slowly cooled steel should be equally hard. Let us consider, for instance, the case of a steel which below the critical range is composed entirely of pearlite, while above this it contains only martensite. Here the martensite and pearlite would have the same chemical composition; they would have the same

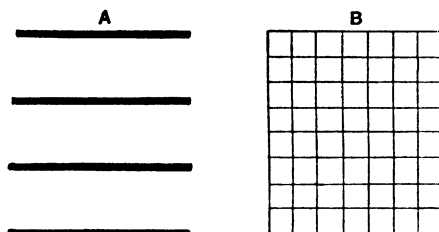


FIG. 1.—STRUCTURE OF PEARLITE.

proportion of iron and Fe_3C . In pearlite, however, the iron and the carbide each segregates in comparatively large masses, while in martensite the hard Fe_3C is uniformly diffused through the whole mass. May not this account for the difference in their mineralogical hardness? To make this matter clear the structure of pearlite, which contains 1 part of Fe_3C to 7 parts of iron, has been sketched in A, Fig. 1, while the structure of martensite can be imagined as appearing somewhat like B.

A and B show the same proportion of intensely hard Fe_3C and of soft iron, but on account of the different structural arrangement and distribution of these two constituents, will not the hardness of martensite, or, rather, its power of resisting abrasion, be much greater than that of pearlite? The relatively large soft areas of the pearlite will be easily scratched or worn away by friction, while the soft meshes of the martensite are on all sides protected by the hard carbide, thus presenting great resistance to abrasion. The soft meshes may actually be so minute that even the point of a needle will be prevented by the surrounding cementite from marking them.

May not the meshes in Fig. 1 be regarded as the submicroscopic ferrite grains of Jeffries and the tiny cementite net as the dispersed cementite particles? Is it not a clear anticipation of the slip interference theory which recently has received much attention? And this was 30 years ago.

The views to be presented here, tentatively and cautiously, appear to me to be in better agreement with observed facts and experimental evidence

as well as with the phase rule, which at least they do not violate. They are based largely on the microstructure of "martensite" needles under very high magnification as brought out by Lucas, on the behavior of austenite on tempering and on the behavior of troostite. They will be concisely expressed.

Austenite is a solid solution of the carbide Fe_3C in gamma iron.

Troostite is a solid solution of the carbide Fe_3C in an allotropic form of iron different from the gamma form and which for the present will be designated as non-gamma iron. The fact that the resolution of troostite



FIG. 2.—STEEL 1 TO 1.1 PER CENT. CARBON; QUENCHED FROM A HIGH TEMPERATURE; ETCHED WITH PICRIC ACID. $\times 3230$. F. F. LUCAS.

Rod was heated at one end to a high temperature and quenched. This field is well toward hard end of specimen and shows very early stages of troostitic development along martensitic needles and as nodules (two of which are seen). Troostite is quite dark, martensite much lighter, austenite white.

fails to reveal the network structure generally found in solid solutions may be ascribed to the grains being submicroscopic, which in turn may explain, partly at least, the hardness of troostite. Lucas finds that what he calls nodular troostite contains radial grains which, under the highest powers of the microscope, exhibit all of the characteristics of solid solutions. When undecomposed, he reports, that these grains consist of a single constituent and that they display orientation phenomena when revolved about the optical axis of the microscope.

Austenite always transforms into troostite on slow or rapid cooling, as well as in tempering after quenching.

In my paper of 1896, I wrote:

While we know with reasonable certainty the composition of ferrite, cementite and pearlite, we know very little about the true nature of martensite. Indeed, if we could discover its composition, the hardening of steel would no longer be an unsolved problem. Each theory which has been advanced to explain the hardening of steel has attributed to martensite the composition demanded by that theory. Of its real composition, however, we have no direct evidence. Unfortunately, the details of its structure are so minute and so difficult to resolve that, even when most highly magnified, it gives little indication of its chemical composition or even structural character.

The remarkable high-power photomicrographs recently obtained by Mr. Lucas have supplied what we were so much in need of 30 years ago and have confirmed my belief in the duplex nature of this so-called martensite.



FIG. 3.—IRON-CARBON ALLOY; 2.65 PER CENT. CARBON; QUENCHED IN ICED BRINE FROM 1260° C.; ETCHED 3 MIN. IN PICRIC ACID. $\times 2450$. F. F. LUCAS

The structure of hardened steel containing from 1.00 to 1.10 per cent. carbon is seen under an original magnification of 3230 diameters in Fig. 2. It is customary to state that the dark needle-like constituent is martensite, itself a solid solution of carbon in alpha iron, and the lighter one, undecomposed austenite. In that light hardened steel must be considered as an aggregate of austenite and martensite. On close examination, however, we note that the steel also contains particles decidedly darker than the so-called martensite needles, and we call these particles troostite, which we describe as an aggregate of finely divided ferrite and cementite. Hence, as already mentioned, the presence of four phases.

Lucas writes: "No evidence has been found that a plain carbon steel may become fully martensitic. The structures at high power are seen to consist of austenite and martensite, but more often of austenite, martensite and troostite, sometimes of even lower orders of decomposition."

In order to study the nature of martensite we may confine our attention to a few needles as they appear under very high magnification, (1) in quenched samples and (2) after prolonged tempering. Martensite needles embedded in an austenite matrix are seen in Figs. 3 and 4, representing the structure of an iron carbon alloy containing 2.65 per

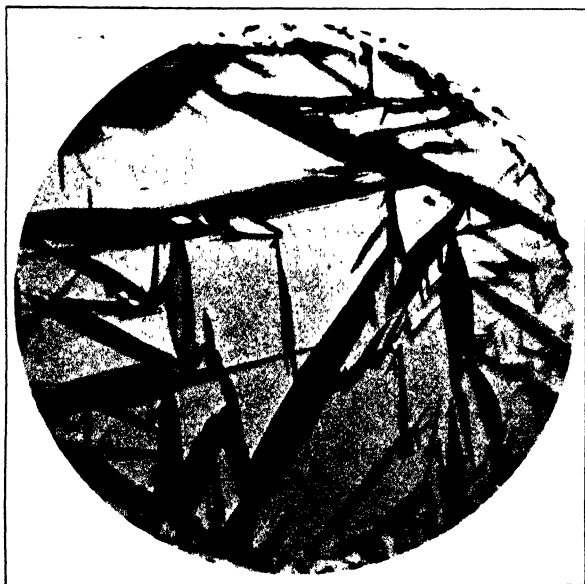


FIG. 4.—SAME AS FIG. 3; ANOTHER SPOT; 1260° C., QUENCHED IN BRINE.

cent. carbon and quenched in iced brine from a temperature of 1260° C. The original magnifications were, respectively, 2450 and 2100 diameters. The conditions are here at their best to study the structure of the needles and the transformation of both the needles and the austenitic matrix on tempering.

We find that the needles themselves are not made up of a single phase but clearly of two phases—that they are therefore of the nature of an aggregate. They all have a central or midrib which is much darker than the surrounding metal. I believe this midrib to be made up of troostite, a solid solution of carbon in non-gamma iron resulting from the allotropic transformation of austenite along its octahedral cleavage planes. I believe the balance of the needles to consist of austenite in which troostite is present too finely divided to be detected even under very high
t quantity to result in a darker coloration of

the needles by etching compared to the color of the undecomposed austenite surrounding it. This transformation of austenite into troostite through the formation of troostite-austenite needles (martensite) along the octahedral cleavage planes of austenite is well illustrated by Lucas in Fig. 5.

My views demand that in tempering, austenite should transform into troostite (a solution of carbon in non-gamma iron), and this, I believe, is precisely what happens as revealed by some experiments² conducted by Lucas. This long tempering of a quenched high carbon steel consisting of martensite needles in an austenite matrix did not result in the formation of additional needles but clearly in additional troostite causing

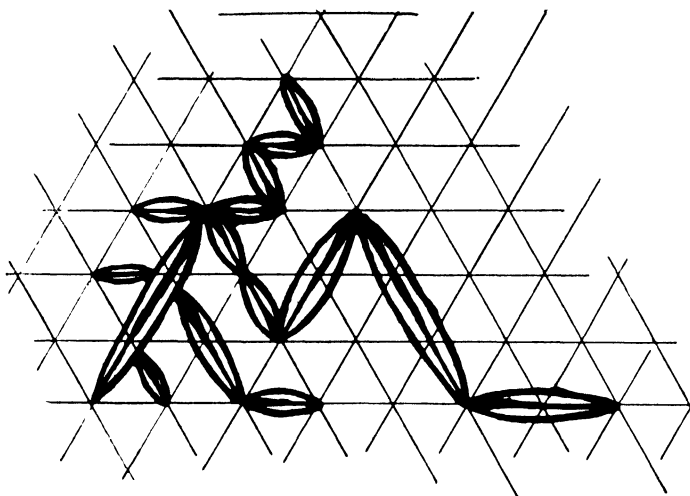


FIG. 5.—DEVELOPMENT OF MARTENSITE ALONG CLEAVAGE PLANES PARALLEL TO SURFACE OF AN OCTAHEDRON THREE SETS OF PLANES. F. F. LUCAS.

the original needles to color darker and in the occurrence of many troostitic fringes around the needles and of troostitic particles in the austenitic matrix.

It should also be noted that while it required three minutes in picric acid to bring out the structure of the sample as quenched, 10 seconds sufficed after the sample had been tempered, a strong evidence of the presence of much more troostite in the latter.

CONDITION OF IRON IN TROOSTITE

Passing now to the important question of the condition of iron in troostite, which I have so far described as non-gamma, our first impulse must be to infer that it is alpha iron. Alpha iron, however, has little if

² The sample which after quenching had the structure shown in Figs. 3 and 4 was tempered by him for 13 hours at 200°C., repolished, re-etched, and again photographed as shown in Figs. 6 and 7, under an original magnification of 3500 diameters.



FIG. 6.—SAME SAMPLE AS ILLUSTRATED IN FIGS. 3 AND 4. BRINE-QUENCHED FROM 1260°C .; TEMPERED 13 HR., 20 MIN., AT 200°C .; ETCHED 10 SEC. IN PICRIC ACID $\times 3,500$. F. F. LUCAS.



FIG. 7.—SAME AS FIG. 6; ANOTHER SPOT.

any dissolving power for carbon, from which it follows that carbide should always be rejected from troostite both on slow cooling and on tempering.

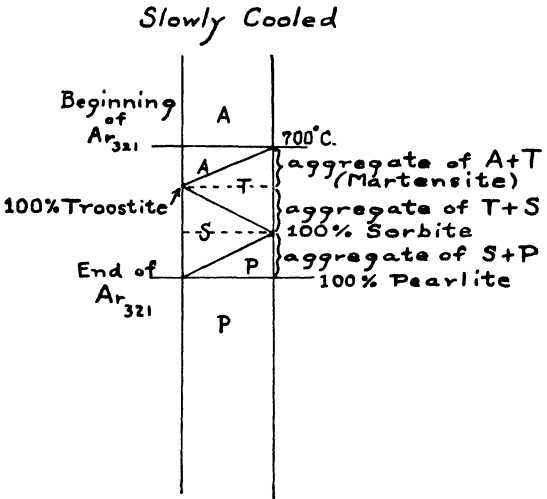


FIG. 8.—DIAGRAM SHOWING TRANSFORMATION OF AUSTENITE INTO PEARLITE.

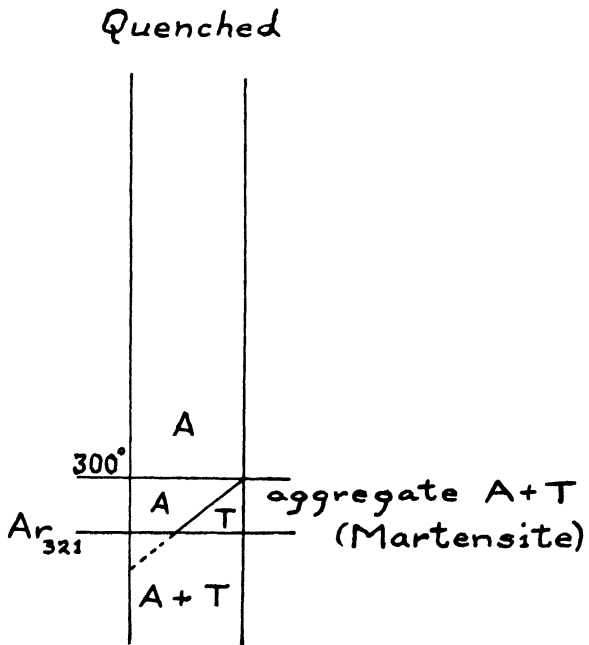


FIG. 9.—DIAGRAM SHOWING TRANSPORTATION IN COOLING AUSTENITE SO THAT THE AUSTENITE-TROOSTITE AGGREGATE IS RETAINED AND THE STEEL IS HARDENED.

Lucas, however, finds that while carbide is expelled from troostite of hyper-eutectoid composition, ferrite is expelled from hypo-eutectoid

troostite, clearly indicating that the iron in troostite is capable of dissolving carbon up to the eutectoid point.

Troostite, in this light, must be considered as a solution supersaturated with carbide when it contains more than 0.85 per cent. carbon. This non- γ iron capable of dissolving carbon I shall venture to call beta iron, although fully realizing that this beta iron may yield an x -ray spectrum similar to that of alpha iron and of delta iron.

This conception of the nature of austenite, troostite and martensite leads us to visualize the transformation of austenite into pearlite as follows:

The complete transformation of austenite into pearlite requires time and plasticity, hence slow cooling from a sufficiently high temperature. Assuming for the sake of simplicity, the steel to be of eutectoid composition, when it enters its critical range, austenite begins to transform allotropically into a solid solution of carbon in beta iron, which, in my opinion, is troostite. Time is required for the complete transformation of austenite into troostite and finely divided aggregates of austenite and troostite are necessarily formed which hitherto have been called martensite and have generally been considered as solid solutions. The austenite-troostite transformation begins along the octahedral cleavage planes of austenite, giving rise to the well-known so-called martensite needles. These needles consist of a midrib of solid troostite surrounded by austenite holding very finely divided particles of troostite. Farther transformation results in the growth of the needles at the expense of the untransformed austenite and in the final complete transformation of austenite into troostite. The next step in the transformation consists in the formation of alpha iron and simultaneously, since alpha iron cannot dissolve carbon, in the rejection of carbide resulting in the formation of sorbite. This is followed by the coagulation of the cementite particles into plates resulting in the production of pearlite. In cooling austenite at such a rate that its transformation is delayed until a temperature of some 300° C. is reached, the austenite-troostite aggregate is retained and the steel is hardened. These views are expressed diagrammatically in Figs. 8 and 9.

SUMMARY

Austenite is a solid solution of carbon, probably in the form of the carbide Fe_3C in gamma iron.

Troostite is a solid solution of carbon, probably in the form of the carbide Fe_3C in beta iron.

Austenite always transforms into troostite regardless of the temperature at which the transformation takes place.

Martensite is the aggregate of austenite and troostite necessarily resulting from the *gradual* transformation of austenite into troostite.

Troostite of eutectoid composition transforms into sorbite.

Troostite of hypo-eutectoid composition transforms into sorbite after rejection of the "excess" ferrite.

Troostite of hyper-eutectoid composition transforms into sorbite after rejection of the "excess" cementite.

The rejection of some cementite from hyper-eutectoid troostite and of ferrite from hypo-eutectoid troostite may take place at room temperature from which it follows that aged troostite may be described as an aggregate consisting of minute particles of the carbide Fe_3C or of ferrite in a matrix of the solid solution of the carbide in beta iron, that is, of true troostite.

The transformation of troostite into sorbite implies the allotropic transformation of beta iron into alpha iron and the formation of a very fine aggregate of alpha ferrite and of cementite.

Pearlite results from the coagulation into plates of the constituents of sorbite.

Gamma iron being unstable at room temperature, austenite, on reheating, tempers into troostite through the transformation of gamma into beta iron and the retention of the carbide in solid solution.

Although beta iron is more stable than gamma iron, troostite, on further reheating, tempers into sorbite through the transformation of beta into alpha iron and the rejection of cementite.

Austenite is harder than gamma iron because it is a solid solution, it being well known that solid solutions are generally harder than the solvent.

Troostite is harder than austenite, possibly because beta iron is harder than alpha iron; also possibly because of the presence in troostite of submicroscopic grains offering greater resistance to slip, the structure of troostite being much finer than that of austenite; because of the distortion of its crystal lattice or, again, because of the existence of severe internal strains.

The hardness of troostite increases with the percentage of carbon it contains, possibly because of increasingly smaller grains.

The aggregate martensite is harder than the troostite it contains and *à fortiori* harder than the austenite because the structural arrangement of these two constituents offers greater resistance to slip than plain troostite. Its very acicular structure favors that view as pointed out by Thompson, who writes, ". . . the needles formed act as strengthening scaffolds throughout the mass."

The hardness of martensite increases with its carbon content because of the greater hardness of the troostite it contains, and possibly also because finer needles and finer grains result from the transformation of austenite containing much carbon.

We are naturally led to inquire into the proportions of austenite and of troostite which should be present in the aggregate martensite in order

to obtain maximum hardness for a given percentage of carbon. The answer may be that we should have as many needles as possible on the ground that the greater the number of needles the greater the slip interference. This would be in line with the increased hardness resulting from an increasing percentage of carbon because as the carbon increases the needles become smaller and hence more numerous.

It is well to bear in mind that although I have arrived independently at the views I have tried to express in regard to the nature of hardened steel, I am not the first who has considered martensite to be an aggregate and not a solid solution, as will be apparent from my brief discussion of the views expressed by eminent metallurgists. Those, however, with the exception of Lucas, who have referred to martensite as being an aggregate, also describe troostite as an aggregate. Lucas believes troostite to be a solid solution and martensite an aggregate of ferrite and cementite, while I consider martensite to be an aggregate of austenite and troostite. Dejean has indicated the possibility of two solid solutions being present in martensite, one of carbon in gamma and the other of carbon in alpha iron, but there is no evidence that he identifies the latter with troostite. Boylston, however, refers to the possible presence of troostite in so-called martensite needles.

Appendix

Following are the full answers received by the author from those to whom he submitted his questionnaire:

EDGAR C. BAIN*

1. Martensite is the product—under certain specific conditions—of the allotropic change undergone by solid solutions of gamma iron. It is characterized by being alpha iron in extremely fine or badly crystallized, although strongly coherent, fragments. It may have a great range of carbon content in a condition not well understood, and is almost always mixed with residual particles of unchanged austenite. From freshly formed martensite the carbide of iron may be precipitated very easily even at room temperature in particles so fine as to offer no clue to their existence save by magnetic tests and shrinkage measurements. This material, containing very fine crystallites of carbide, is also called martensite.

The characteristic needlic structure is the result of the directional nature of the allotropic change and is determined by orientation of the parent austenite.

Martensite is hard because of the tremendous slip obstruction of both the small or badly crystallized alpha iron grains, and the tiny carbide particles subsequently developed.

2. The conditions necessary for the formation of martensite from austenite are merely, first, such temperature as renders alpha iron the stable form and gamma iron unstable and, second, a degree of atomic mobility (and time) sufficient to permit the allotropic rearrangement of atoms *but not* any substantial grain growth. The removal of heat from a specimen at a proper rate is the customary manner of providing the limited mobility of atoms. Cold work supplies the same requisite atomic mobility when applied to preserved austenite.

The writer has described a possible simple atomic shift which would change gamma iron to alpha iron along plates corresponding to gamma iron crystal planes. As yet that explanation is as reasonable as any but is purely speculative.

3. Mechanically, freshly formed martensite may resemble a true solid solution of carbon in alpha iron, but it probably should not be called simply a "solution," since a solution is usually thought to be stable unless definitely designated "supersaturated" or "under-cooled." It is not known just where the carbon atoms are located in reference to the alpha iron space lattice, but the evidence points strongly to interstitial spaces and not the customary lattice points usually occupied by solute atoms.

4. Strains play a vital part in the hardening of steel in so far as the pieces crack and break in the quench or subsequently; otherwise, except for a possible action to decrease the amount of residual austenite in proportion to their severity, they probably have nothing to do with the hardening. They are an effect, not a cause.

COL. N. BELAIEV†

1. Martensite is the hard constituent of quenched iron-carbon alloys. The so-called "acicular" structure of martensite is a Widmanstätten structure. Its needles

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† London, Eng.

or, more correctly, wedges run parallel to the four faces of an octahedron in every martensitic grain. There is, apparently, a slight difference in hardness and in carbon concentration between different wedges, but, in general, their nature is one and the same. Thus, the occurrence of the Widmanstätten structure is caused not by a chemical differentiation, as in slowly cooled steels or in meteorites, but by the physical process of deformation during rapid cooling.

There is a certain analogy between the formation of slip bands in various grains of a statically deformed specimen and the martensitic structure of quenched steel. In both cases are the structures revealing a deformation which occurs parallel to the octahedral planes. In the former, the slip bands usually show one direction only; however, as the amount of deformation increases the number of "directions" increases too, till the four directions duly appear. Thus the appearance of all the four directions in martensite may, conversely, be taken as a proof that the whole potential amount of deformation inherent in any and every martensitic grain has been exhausted—whence its hardness.

2. The conditions necessary for the formation of martensite can be summarized thus: any sudden change in internal pressure revealing itself in a more or less simultaneous gliding on the octahedral planes. Such conditions can be realized best by the action of interatomic forces during a sudden allotropic transformation.

During quenching the gamma-alpha transformation takes place suddenly and, more or less simultaneously in every grain. This transformation results in a considerable increase of volume as the face-centered lattice changes to the cube-centered. The increase of volume in and of every grain is interfered with by the boundaries of the grains—thus considerable strains originate and result in producing the maximum available deformation parallel to the four octahedral planes in every grain.

The resistance to any considerable amount of future slip is very much increased and so is the so-called hardness.

3. According to the latest x-ray evidence the carbon atoms occupy the central points of the cubes in the face-centered lattice of gamma iron. Such structure corresponds to what has been called a solid solution of carbon in iron or austenite.

As the face-centred lattice changes to the cube-centered the carbon atoms have to be displaced from their initial central positions. The larger the carbon content the greater the number of carbon atoms to be displaced. Thus, very likely, the space of time available for the change of lattice—at any given speed of cooling—is lessened in ratio to the amount of carbon atoms to be displaced and redistributed. Consequently, the occurring internal stresses will be the larger, the higher the carbon content. The fact that the lattice dimensions of austenite increase with the carbon content will work in the same direction.

The actual position of carbon atoms in martensite has not been definitely shown by the x-ray examinations. As, on the other hand, both the x-ray and the former metallographic investigations have proved that iron in martensite must be present in the alpha state, it would seem that the iron particles are free from carbon. Thus the carbon atoms must be distributed in martensite in some different way from that which exists in the true solid solution-austenite. Some authors therefore consider martensite as a supersaturated solution, while some others regard it as a colloidal system. The present writer still considers that the true colloidal state occurs in troostite and the state of solid solution in austenite. For martensite he would prefer for the present to use a descriptive phrase, such as "as if in solution" or the term "pseudosolution."

4. Internal interatomic strains resulting from the sudden gamma-alpha transformation during quenching are responsible for the Widmanstätten acicular structure of martensite and, finally, for the main part of its hardness, a certain increase of hardness may be caused by the grain refinement and by the, so-called, key action.

Internal intercrystalline strains may be responsible for the larger or smaller amount of gamma iron changed to alpha iron.

CARL BENEDICKS*

1. Martensite is a solid solution of carbon, "free" or "combined," in alpha iron; its hardness is due to the disturbance of the alpha lattice caused by the solute having a low natural miscibility with alpha iron.³

2. Martensite is formed on dissolving carbon, "free" or "combined," in gamma iron and then cooling, at a rate permitting the carbon to be preserved in solid solution, while the solvent is changed from gamma into alpha state.

3. As has been established by A. Westgren and G. Phragmén,⁴ the carbon in austenite does not substitute iron atom for atom in the gamma lattice; consequently, in gamma iron, carbon is to be designated as being probably combined, or forming radicals, with iron atoms. As for martensite or alpha iron nothing has been definitely established, but it seems probable that carbon occurs in the same way.

4. The hardening of steel being due to forcing a less soluble substance to remain in solution, it is necessarily accompanied by strains in the crystal lattice (see note 1); on the contrary, the earlier debated strains due to the difference in cooling speed between the inner and outer parts of a quenched specimen has no essential influence on hardening.

HERBERT M. BOYLSTON†

1. In my opinion martensite is a mixture of a solid solution of iron carbide in beta iron and some alpha iron, probably in the form of troostite. I am inclined to think that the dark parts of the martensite needles are troostitic in character, although I am not at all sure that the mixture can be resolved into constituent parts except possibly under extremely high magnification.

2. I think the conditions necessary for the formation of martensite are a rate of cooling of steel sufficiently rapid to lower the transformation point temperature to approximately 300° C. or lower. A sufficient amount of alloying material with the proper rate in cooling might act in the same way but the point of the *whole* matter is, in my opinion, that the rate of cooling through the critical range, whether it occurs at the usual temperatures or at lower temperatures, be rapid enough to retain below its normal region the solid solution of Fe₃C in Beta iron.

3. I cannot answer this.

4. I do not know.

HARRY BREARLEY‡

1. Martensite is carbide dissolved or finally dispersed in alpha iron.

2. Martensite is formed from austenite on cooling from high temperatures when the gamma to alpha change takes place in the iron and the medium is too rigid, owing to accelerated cooling, to permit the dispersed carbide to aggregate.

* Director, Metallographic Institute, Stockholm, Sweden.

³ C. Benedicks: *Recherches Physiques et Physico-chimiques sur L'acier au Carbone. Thèse Upsala* (1904) 202, where it was concluded that martensite is a solid solution in beta iron; it being later shown that beta iron probably is alpha iron containing a definite amount of gamma iron (cf. *Jnl. Iron and Steel Inst.* (1912) **2**, 242). Beta has to be replaced by alpha as is also directly established by x-ray analysis.

⁴ A. Westgren and G. Phragmén: *X-ray Studies on the Crystal Structure of Steel. Part II. Jnl. Iron and Steel Inst.* (1924) **1**, 159.

† Professor of Metallurgy, Case School of Applied Science, Cleveland, O.

‡ Brown Bailey's Steel Works, Ltd., Sheffield, England.

3. I do not know.

4. Stresses and strains are important causes of hardening, but I cannot make any quantitative estimate of their influence.

WILLIAM CAMPBELL*

In reply to your letter of Aug. 17, I am afraid that I do not know enough about martensite and the causes of its hardness to make my reply to your question of any value. For the last few years I have been teaching Jeffries' and Archer's slip interference theory of hardening. However, I do have some difficulty in accepting their theory that part of the reason for its hardness is extreme fineness of grain, especially after examining a high carbon steel quenched in very high temperature.

1. Martensite is ferrite or perhaps alpha iron, with a small amount of carbon in solid solution, and containing iron carbide in a very fine state of dispersion, and this iron carbide is the cause of hardness due to slip interference.

2. It is formed by the decomposition of austenite at a temperature considerably below the lower critical point.

3. I do not know enough about atomic structure to be able to answer this question.

4. I do not think that strain plays any material part in the hardening of steel.

PIERRE CHEVENARD† AND ALBERT PORTEVIN‡

Definition.—Martensite is a solid solution, in which iron is in the alpha condition, and which corresponds for a given percentage of carbon to maximum hardness. It is a metastable phase of the iron-iron-carbide system. Its composition varies and, therefore, its physical properties cannot be numerally defined.

Micrographical Characteristics.—It is not colored by oxidizing alkaline reagents such as sodium picrate, being in this way distinguishable from cementite. It is colored by acid reagents such as picric and nitric acid, somewhat like ferrite and austenite but in general a little more than ferrite and less than austenite, which distinguishes it from the aggregates pearlite, troostite, and sorbite. It is colored by cupric reagents such as Stead's and Le Chatelier's much less than ferrite.

The scratch produced by a needle is of minimum width; it cannot be scratched by a quenched needle having the same composition as the steel examined, by which it can be distinguished from ferrite and austenite. The latter constituent may also be distinguished by the presence of slip bands after slight deformation.

The needle-like appearance frequently mentioned as an essential characteristic of martensite is not absolute; on the contrary, it occurs more clearly when martensite is not pure, as, for instance, in quenched mild steels (martensite mixed with ferrite), or in high carbon steel drastically quenched (martensite mixed with austenite). It disappears in eutectoid steel quenched so as to obtain maximum hardness, and made up, therefore, of pure martensite. One must distinguish carefully between the martensitic *state* and the martensitic *appearance* described as needle-like, which is a type of structure closely connected with the Widmanstätten formation and which occurs whenever a constituent separates progressively from a phase or solid solution (especially in all transformations of alloys in which only two phases occur). As martensite, however, is very rarely pure, this appearance is frequent, and as it is revealed readily by etching, its use is convenient.

Physical Characteristics.—These characteristics can be fully utilized only when martensite forms the totality or the major part of the sample. In martensite, carbide

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is in solid solution, iron in the alpha condition, and the density is minimum because of the marked expansion taking place when alpha iron forms. Hence the following characteristics:

1. No sudden evolution of heat on heating.
2. *Minimum density*; on heating, dilatation nearly equal to that of alpha iron; *absence of the Curie A_0 point of cementite at about 200°C .*, followed by *notable and progressive contraction* resulting from the precipitation of carbide.
3. *Maximum resistivity*, depending upon the percentage of carbon.
4. *Ferro-magnetism*: Without any Curie A_0 point of the carbide at about 200°C .
5. *X-ray analysis*: Cubic crystalline system dodecaedric (face-centered cubes) of alpha iron.

Mechanical Characteristics.—Maximum hardness exceeding 600 Brinell in ordinary steels when the percentage of carbon exceeds .50 per cent.

CAUSES OF THE HARDNESS OF MARTENSITE

This question which has already resulted in the flowing of so much ink has never, I confess, interested me much. One might as well ask why diamond is much harder than graphite and what is the cause of the white or red coloration of phosphorus.

I have been satisfied with observing some facts and in seeking experimental relations which could be defined and measured and which exist between the various factors influencing hardening and the results of that operation. I am satisfied with the observation that the increase of hardness which results from the presence of martensite corresponds to the presence of a constituent the characteristics and nature of which do not result in contradictions with known facts.

Martensite is a crystallized solid solution which forms on cooling through the transformation at a low temperature, accompanied by a notable expansion. Hence the following internal modifications:

Maintenance of the carbon in solid solution (physico-chemical modifications).

Refining of the grains, formation of twins and strains (structural modifications).

Occurrence of intense internal strains.

Experience has taught us that each one of these modifications considered separately may result in an increase of hardness. In accordance with our tastes and personal tendencies, we attribute to some of them a preponderating or exclusive part in the increase of hardness. Hence, we have as many theories of hardening as of observed phenomena.

Since until now it has not been possible to measure and to characterize these various modifications and their effects it seems to me difficult to test the part of each in this increase of hardness.

For the time being, therefore, these are simply exercises of the mind which have some success because they give free play to the imagination. One sees in it a proof of the predilection for explanations borrowed from mechanical science.

It is apparent that for many, because of their tastes and their intellectual training, mechanical representations applied to geometrical edifices even complex, satisfy their mind more than the application, pure and simple, of the facts. The History of Science presents many such examples. According to H. Poincaré, as soon as a phenomenon obeys the principles of energy it conforms with an infinity of mechanical explanation.

Summing up, one tries to connect the increase of hardness with other facts considered simple because they are observed daily and because habit makes us accept them more readily and makes us consider them as fundamental truths.

As the experimental proofs of the accuracy of these conceptions appear to me for the moment difficult to produce, one may define with more or less ingenuity one or

another explanation while being certain that he will not meet with serious objections. One may in this way go on arguing indefinitely, and it is this which for some has the charm of diversions which are more metaphysical than physical.

One remains in the domain of hypothesis. Not that I deny the part of these in science, where indeed it is considerable, but they are of real interest only as they are fruitful in provoking research, and I seek in vain what has been until now the usefulness of these hardening theories in adding to our knowledge as well as in the progress resulting from their application.

CONDITIONS OF THE FORMATION OF MARTENSITE

Martensite is formed when the transformation on cooling takes place at a low temperature without recalescence (point Ar''). If the external conditions which regulate the law of cooling are not modified during cooling, the higher limit of Ar'' may be placed at about $350^{\circ}C$. It has been possible to observe the formation of the aggregate troostite with recalescence at a low temperature (350°) in modifying suddenly the law of cooling through the removal of the sample from the quenching bath (interrupted hardening).

This formation of troostite from austenite with evolution of heat is also observed on reheating for tempering certain steels which have been drastically quenched. On the other hand, martensite may be formed through the tempering of austenite during cooling following the separation of carbide on heating (secondary quenchings).

Considering the case of a simple quenching, that is to say, the gradual cooling of a steel from a temperature exceeding the transformation temperature on heating, the formation of martensite will depend upon the following factors:

Kind of steel and structural conditions before transformation.

Temperature and length of heating.

Rate of cooling.

The influence of the two principal factors, namely, heating temperature and rate of cooling, the other factors remaining constant, may be thus expressed:

1. For a given temperature martensite is formed when the rate of cooling exceeds the *critical speed of quenching* causing a part at least of the transformation on cooling to take place at the low temperature Ar'' .

2. For a given rate of cooling, martensite is formed when the temperature on heating exceeds the corresponding *critical quenching temperature*. This double condition may be expressed by the curve characteristic of the quenching of any given steel. (See Portevin and Chevenard.)

The conditions of the formation of martensite resulting from these characteristic quenching curves must be modified when the structures are initially coarse or abnormal, and also in the case of complex laws of cooling.

Finally, pressure must play a part in the formation of martensite as it does in all transformations accompanied by a change of volume. At present, however, the importance of these instantaneously developed stresses during cooling, and therefore their influence, cannot be measured. This role of pressure seems to be indicated by the differences between the critical speeds of quenching of some wires and some cylinders and also by the occurrence of martensite in the center of the troostitic regions of quenched samples.

MECHANISM OF THE FORMATION OF MARTENSITE

The solid solution gamma or austenite may result in two transformations yielding two states of different stability, namely, gamma solution into pearlite, troostite, or sorbite, and gamma solution into an alpha solution or martensite.

The second state is less stable: it is metastable, compared to the first one, and therefore can be produced only in case of surfusion.

The mechanism is entirely comparable to that of the solidification of cast iron which may result in a metastable condition involving the formation of carbide of iron, and which can take place only in case of surfusion.

In applying the Bancroft-Ostwald rule, one may assume that an intermediate metastable state is formed, namely, carbide of iron in the graphitic solidification of cast iron, martensite in the pearlitic transformation of steel. The direct experimental proof, however, of this transitory martensitic stage has not been obtained, and this hypothesis is at the time useless.

The mechanism of this phenomenon, therefore, is in no way peculiar and is in accordance with the behavior of metastable states. One should not go so far, however, as to apply the intervention of these metastable martensitic states to all the quenching phenomena observed in metallic alloys such, for instance, as duralumin.

3. *Crystallographic Structure of Martensite*.—Not having personally studied x-ray analysis, I can only refer to the conclusions of those who have done work in that direction.

4. *Influence of Strains*.—My opinion on this subject is expressed in my answer to question 2.

I will only call attention to the fact that the hardness resulting from the quenching of alloys and which always appears to be correlative with a transformation at a low temperature is not necessarily accompanied by an expansion as is the case of martensite. It may correspond to a contraction (alloys of gold and copper). In dealing with hardening through strains, therefore, these two cases should be considered. The tensile strength of steel produced by cold working after quenching and tempering and by a martensitic quenching, is practically the same in both cases.

The similarity between the effects of cold working and of martensitic quenching is qualitative only in the case of the hardness, the elastic properties, the refining of the structure, and the density. It no longer exists in regard to the essential physical characteristics of martensite, namely, absence of point A_0 , high electrical resistance. Moreover, the experimental study of internal strains shows that there is complete reversal in their re-partition when the strains created by rapid cooling are compared with those resulting from cold working.

Under those conditions this interpretation can only be satisfactory to those superficial minds possessed by the demon of analogy.

P. DEJEAN*

1. All the tests performed with martensite, such as determination of the discontinuity of ferro-magnetism, dilatation at 210° , x-ray examinations, etc., agree in showing that in that constituent iron is to a great extent in the alpha condition and that there is no free carbide present. On the other hand, seeing that the decomposition of martensite by gradual heating never yields graphite, but solely cementite and ferrite, it is logical to infer that martensite is a solid solution of carbide in alpha iron.

There is one point, however, which should receive our attention, namely, that from a microscopical point of view, martensite does not give the impression of a homogeneous constituent. Under very high magnification, one distinguishes clearly a needle-like constituent on a clear background. There seems to be two phases. As to their nature, several hypotheses may be offered. One might wonder if they are not two "solutions" of the carbide Fe_3C , one in gamma iron (austenite), and the other in alpha iron. It is not impossible, however, that in both solutions the carbide should

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be dissolved in alpha iron and that the only difference would consist in the percentage of carbide dissolved—in the same way that the solutions camacite and taenite of meteoric irons differ only by the proportion of nickel dissolved in the iron.

All this tends to prove that the mystery of martensite is not yet completely solved.

In regard to the hardness of martensite, it is probably closely related with its method of formation at a low temperature.

2. When steel is cooled from a sufficiently high temperature the allotropic transformation of gamma iron (Ar_1) and the separation of the carbide from the solid solution (Ar_1) which is a consequence of it, occur at temperatures which are the lower the greater the passive resistances. These resistances are increased either by the speed of cooling, by the addition to the steel of a certain number of special constituents (nickel, magnesium, chromium, tungsten, etc.), or through a number of other causes but little known at the present time—such, for instance, as the more or less advanced dissociation of the dissolved carbides.

As the rigidity of the metal increases as the temperature falls, and as the transformation at the point Ar_1 as well as that at the point Ar_2 includes increases of volume, a point is reached when the temperature to which the passive resistances have lowered these points is too low to permit the normal transformation to take place. They are completely or partly suppressed, and the metal is preserved out of equilibrium. The difficulty, however, of maintaining it in that state is the greater the lower the temperature, because the tendency of the metal to return to a state of equilibrium increases as the temperature is lowered. A point is reached, therefore, when although the rigidity of the metal is too great to permit the allotropic transformation of the iron with separation of carbide, as takes place at the point Ar_{321} , it is not sufficient to prevent a partial return to a state of equilibrium. It is in this way that at about 250° (a point which may be designated by the symbol Ar'' or by the letter B) the allotropic transformation gamma to alpha can take place without obliteration of the solution of the carbide.

3. As I have not taken up the spectrographic study of martensite, by x-rays, I have no personal opinion in regard to the positions occupied by the carbide molecules in the crystalline structure of alpha iron.

4. It cannot be denied that cold working and quenching often impart to steels very similar properties. It is also probable that the formation of martensite which takes place at a low temperature accompanied by an important change of volume, produces in the steel tensions of an order comparable to those resulting from cold working. One should avoid, however, carrying too far the resemblances between these two phenomena.

G. GRENET*

1. As I do not know the exact definition of martensite, I do not know the characteristics by which it can be defined. The experimental fact is that all the very fine aggregates to which the name of martensite is given, result from a transformation with change of phase at a low temperature.

The relation between cause and effect independently of all hypotheses which bind the low temperature transformation with the hardness and the fineness of structure is the important fact by which hardening is characterized.

As for the cause of hardness, I must be more reserved. I would be inclined to say this: When the elements of a phase are very small the atomic attraction of the components of an element of a phase is noticeable at the center of neighboring elements. The distinction between structural equilibrium and physico-chemical equilibrium disappears in this way in a continuous fashion as the structure of an aggregate becomes finer.

*.Paris, France. Translation.

This extreme fineness at which structural equilibrium ceases to be distinguishable from the physico-chemical equilibrium characterizes, in my opinion, the colloidal state, and the term colloidal aggregate is better suited, in my opinion, to the aggregates designated as martensite than to the aggregates called troostite and sorbite.

When this extreme fineness is reached, whether the distinct crystallites belong or do not belong to the same type, any mechanical action tending to increase the absence of equilibrium meets with a great resistance, whence the hardness.

2 The condition necessary to the formation of a very fine and very hard aggregate (martensite) consists in the transformation with change of phase at a temperature low enough to make it impossible for the elements set free to reassemble again. This temperature varies with different alloys.

In quenching most steels, the aggregate is formed through the decomposition of a phase supersaturated with its two constituents. In hardening copper-aluminum alloys rich in aluminum, the aggregate results from the elimination of one element only from the supersaturated phase. It is natural that the appearance of aggregates formed in such different conditions should be different.

3. To those who say that martensite is the alpha phase supersaturated with carbon, I generally make the following objection: It is surprising that that phase alpha supersaturated with carbon is easier to produce when it contains 1 per cent. carbon than when it contains only traces of it. It is also surprising that what leaves the solution most readily is iron.

Without being too affirmative upon this point, it seems to me that it is more logical to consider hardened steels as being formed of several types of crystalline elements, rather than of only one type.

It seems to me likely that during the low temperature transformation, the element ferrite, which separates in greater mass than the element cementite and which is more malleable, crystallizes in larger elements than the element cementite, admitting that these elements are formed. The element ferrite, moreover, is already very small and one may suppose that the cementite elements are too small to present a number of rectilinear planes large enough to permit the character of cementite to be detected by x-ray analysis.

One of the observations which contributes most to create a distinction between martensite and other aggregates, and to the consideration of martensite as a homogeneous phase, is that of the discontinuity of the transformation during cooling on quenching.

Taking up again, in a modified form, a conception of Osmond, one sees in that discontinuity a separation of two distinct transformations and one of these transformations, the one which occurs at a low temperature, corresponds to the formation of a homogeneous phase or solid solution. This discontinuity, however, is not confined to steel. It may be observed in the rupture of all unstable equilibria. As many discontinuities as one wishes may be observed by adopting a suitable law of quenching and also in many cases (especially with carbon steels) continuity may be observed.

4. I have formerly attributed the hardening to a congenital cold working of the elements set free in the metal in a non-malleable matrix and at the same time I have indicated the possibility of the influence of the fineness of the structure. I am today inclined towards the latter hypothesis. There exists, however, between the quenching phenomenon and the cold working phenomenon a very sharp parallelism.

Hardening by quenching takes place only if the transformation temperature is low enough and therefore the metal lacking enough in malleability to prevent the elements set free from reassembling.

Hardening by cold working takes place only when, at the temperature at which the metal is deformed, it is sufficiently deprived of malleability to prevent the disorganized and dispersed elements to reassemble.

LEON GUILLET*

1. Martensite seems to me to be alpha iron plus some gamma iron containing carbon in solution. The very small size of the constituents explains the hardness.

2. In order that martensite be formed in an alloy, a eutectoid must be present and the speed of cooling must be sufficient to lower the transformation point to about 350° C. One may, therefore, regulate accordingly the quenching temperature or the quenching bath.

3. No answer.

4. Strains play a very small part in quenching.

SIR ROBERT HADFIELD†

1. Martensite (martensitic structure) is believed to be a solid solution of carbon or carbide of iron in alpha iron.* Sufficient evidence does not seem to have been accumulated that would enable anyone to determine definitely what is the cause of the hardness of martensite (martensitic structure), or whether the carbon, when in solid solution, exists as atoms of carbon or molecules of Fe_3C .

2. The condition necessary for the formation of martensite (martensitic structure) is that the liberation of internal energy should be partially suppressed, and this is achieved by causing it to take place at a lower temperature than when it is allowed to take place freely.

The mechanism of this formation is not fully known, but appears to be connected with movement along the cleavage planes of the allotriomorphic crystals.

3. As to the position of the carbon in the space lattices the evidence does not seem to be conclusive.

4. Cases are well known in which stress alone, resulting in strain but without alteration of lattice, is sufficient to produce a considerable increase in the ball hardness of certain steels. On the other hand, it has not been conclusively determined whether the presence of strain is always a necessary condition of the hardening.

W. H. HATFIELD‡

1. As regards the nature of martensite and the cause of its hardness, I should answer that my belief is that the essential characteristics of martensite are, firstly, that it is intensely hard, and secondly, that it is largely a solid solution. It would appear that the cause of its hardness is due to the fact that it is essentially, though not completely, a solid solution. One outstanding experiment of my own, which I never published, consisted of taking a heating curve of the hardened state of steel by the differential method. It is very difficult experimentally to determine exactly the relative amounts of heat evolved, say, in cooling a carbon steel reasonably slowly through the critical point and the amount of heat evolved on heating a hardened piece of the same steel. My attempt, however, to make this comparison, put me in the possession of the knowledge that on heating hardened steel there is an evolution of heat approximately of the same order as the evolution of heat when normally passing through the carbon change point. This is, therefore, a fundamental fact of very considerable

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‡ It will be noticed that in giving the answer to question 1, alpha iron is mentioned. This is necessary as the distinction between martensite (martensitic structure) and austenite, or austenitic structure, is that between alpha and gamma iron, as confirmed by the x-ray methods of Sir William Bragg.

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importance, and it does mean that any modification that has been wrought in the solid solution condition existing at high temperatures by the sudden quenching, although still existing in the solid solution state, has, from the physical chemistry point of view, been of a much less magnitude than is held by many people in considering this question. The very considerable evolution of heat to which I have referred, which occurs during the heating of hardened steel, suggests the preservation of the solid solution state existing at high temperatures before trapping, but against this deduction one has to apply the more important fact that martensite is definitely magnetic, whereas the gamma solid solution is non-magnetic. We also have to place along with this latter fact the recently determined x-ray observations which suggest that, according to this method of attack, the iron in hardened steel is in the crystalline form associated with the alpha phase.

The magnetic characteristics of martensite, while in themselves not necessarily indicating the alpha phase, must be taken to do so when supported by the results of x-ray crystal study. It would, therefore, definitely be deduced from the above that from the evolution of heat given up by the martensite it is a solid solution, and from the other evidence, that it is a solid solution in alpha iron. It is, however, clear that such a deduction simply corresponds to our present state of knowledge.

As regards the cause of the hardness, I am led to the view that if the martensite were a simple solid solution it would not possess its great hardness, and it well may be that it is not a simple solid solution, and that, owing to its being only a metastable phase, if indeed it can be considered a phase, the arrest of a transformation before completion may, and indeed almost certainly will, result in a great internal stress and extremely small crystal structure. I should, therefore, put down the hardness of martensite as being due to a combination of internal stress and very small crystal structure.

2. The condition necessary for the formation of martensite is that the steel shall be heated above the temperature at which the carbide goes into solution and shall then be cooled at a critical rate. Carbon steels do not, within my experimental experience, lend themselves for a proper study of the formation of martensite. The change from the solid solution, once it begins to take place, is very rapid. If, however, other elements are added to the steel, the change from the solid solution takes place more slowly, although it is somewhat begging the question to consider, as we do, that a strict analogy may be made between a steel heavily charged with other elements and a plain carbon steel. If, however, we agree that it is correct to work by analogy, then undoubtedly there are steels such as high chromium steels and the high nickel steels, the result of the quenching of the solid solution of which, leads to the production of an extremely ductile condition of the steel which is in no sense hard. Such quenched conditions of alloy steels do, under the x-ray method of attack, give evidence that their crystal structure is dissimilar to that of the alpha phase. Also, and here I would refer you to an article of mine which will appear in the *Metallurgist*, the supplement to the *Engineer*, this autumn, probably in September: this soft gamma state of alloy steels will, under a cold-work effect, be converted into a crystalline condition identical with that of alpha iron. It is also a fact that such alloy steels, after quenching in a solid solution condition, will, on tempering at gradually ascending temperatures, yield a hardness, which, if it cannot be considered equivalent to the hardness of a characteristic martensite, undoubtedly approaches in that direction and thus yields the alpha phase. From these observations you will see that my deduction is that martensite is the intermediate product between the real solid solution existing at high temperatures and the ultimate soft condition of the alpha state.

With regard to the mechanism of the formation, I think it is to be inferred from what I have already said, that the actual mechanism can be described as an arrest in the transformation of one phase to another as discussed under question 1.

3. This question takes one much further into the realms of theory than the foregoing but I should emphatically state that it is my opinion that the carbon is in solution as carbide, Fe_3C or some chemical equivalent. I do not think I will go to the length of explaining why, but it is quite clear that if carbon is placed in contact with iron at elevated temperatures, Fe_3C is formed: that is a definite and established fact. When carbon separates out of solution it falls out as Fe_3C , and I would refer you to a paper of mine in the *Proceedings of the Royal Society*, Vol. 85, 1911. This is my understanding of the matter. I am well aware that this subject in itself may be discussed at great length and that a very good case could be made in the opposing direction. Having asserted that I believe the carbon to be in solution as Fe_3C , it is then necessary, to answer your question, that I describe how the atoms of the carbide molecules should be placed within the crystal. Here I must confess that much as I have endeavored to familiarize myself with the space lattice arrangement of the atoms, I have not yet obtained from the pure physicists an adequate conception of the possibilities in this direction. In the first place, one must obtain a much more familiar knowledge of the atom itself before one's conceptions can take definite shape. However, if one again accepts, and I believe one is entitled to do so, the view held by physicists on this particular aspect, it might be reasonable to assume that the iron atoms of the carbide aggregate tend to take up positions on the normal space lattice of the iron, the carbon atoms being probably situated inside the normal space lattice of the iron atoms.

4. I have already said that I think that the internal stress, and probably also permanent strain effects resulting from quenching, play a very important part in the production of the hardness, and this, in my opinion, is confirmed by the fact that a martensitic condition of steel, if tempered at a low temperature, i.e., a temperature below that at which, so far as we know, the constitution can be modified, the hardness becomes less and the ductility greatly increased.

SAMUEL L. HOYT*

1. My opinion of the nature of martensite is practically as given in the Hanemann-Schrader paper of 1925. The hardness is due to the phase of about 0.9 per cent. carbon in which the carbon and iron are in forced solution or combination. The high mineralogical hardness would be due to the new interatomic bonds which are thereby set up.

2. Martensite forms when austenite is quenched sufficiently rapid to retain the gamma iron solid solution down to about 300 to 350° C. At that temperature austenite changes to what we call martensite. The mechanism is about as given by Hanemann and Schrader.

3. After calculating the number of atoms of carbon which may replace the iron atoms in the body-centered cubic lattice, and given the density and lattice parameter, as measured, my opinion is that a 0.9 per cent. carbon martensite has about half its carbon atoms in the lattice and the other half of its carbon atoms in the interstices. No cause for such an atomic arrangement is known to me and it may be found later, contrary to this picture, that the distribution is simple.

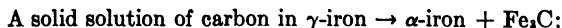
4. Due to the fact that hardening involves an appreciable volume change, I believe that strains must play an important rôle in the process through the pressure effects which they will set up. If the pressure distribution were known, the effect would be that predicted by applying the principle of Le Chatelier.

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KÔTARÔ HONDA*

1. Martensite is a solid solution of carbon in alpha iron, or atomistically expressed, it has a body-centered cubic lattice as in ferrite, but with carbon atoms in the interspace of the lattice.

2. From the viewpoint of the x-ray analysis, the A_1 transformation in steels consists of the changes:



or, iron atoms of gamma solid solution first change their configuration from a face

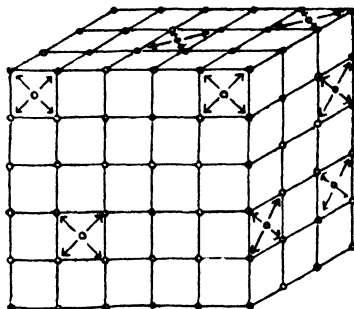
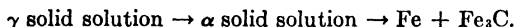


FIG. 10.—DIAGRAM SHOWING POSITION AND DISTRIBUTION OF CARBON ATOMS IN BETA MARTENSITE.

centered into a body-centered cubic lattice, carbon atoms being still in the interspace between the atoms, and then the separation of carbon as the cementite from the solid solution follows immediately. Or, symbolically expressed:



That is, the A_1 transformation consists in its process of:



During a very rapid cooling, such as quenching in water, the first change from austenite to martensite is so far retarded that it begins to take place at a temperature below 300°C ., and when this change is completed, the specimen which is subjected to this treatment is nearly at room temperature, and hence the second change from martensite to pearlite cannot take place owing to the great viscosity of the specimen at room temperature. Thus the martensite can be obtained by quenching the steel in water.

3. Recently it is confirmed that there are two kinds of martensite, which can be tempered at two different temperatures, about 180° and 340° ; the one (alpha) is more easily etched than the other (beta).

Carbon atoms in beta martensite very probably have their position in the center of the face of an elementary cube, distributed here and there according to the law of probability, as shown in the annexed Fig. 10. On the other hand, carbon atoms in alpha martensite have probably their position midway between a corner and the body-center in the diagonal of the unit cube, also scattered at random here and there according to the concentration of carbon. This position is not so stable as that above referred to; that is, alpha martensite is less stable than beta martensite. These con-

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figurations of carbon atoms behave themselves like diagonal supporters in a square framework, giving to the lattice-building a great strength as a whole, which explains the real meaning of the so-called "hardening carbon."

4. Undoubtedly the martensite is undergoing a great internal stress, and hence the natural hardness of martensite is increased by the stress as in the case of cold-work. It is estimated that the increase of hardness due to the internal stress does not exceed 150 in Brinell scale. Also the fineness of martensite crystals increases the natural hardness of martensite. By "natural hardness" we understand the hardness of a single martensite crystal, which does not undergo any stress. According to my view, at least $\frac{2}{3}$ of the great hardness of martensite (650 in Brinell scale) is due to the effect of the hardening carbon as explained above, that is, carbon atoms present in the interspace of the lattice.

ZAY JEFFRIES*

1. I believe that freshly formed martensite in carbon containing steel is fine grained ferrite, crystallizing with a body-centered space lattice, in which the carbon is largely atomically dispersed, and that the hardness is due principally to the grain refinement but partly to the carbon. In aged or tempered martensite the carbon may be partly or even largely associated to form myriads of minute particles of iron carbide partly within ferrite grains and partly at grain boundaries. The maximum hardness will probably occur at a certain stage of association of the carbon.

2. I believe the main condition necessary for the formation of martensite in carbon containing steel is the suppression of the transformation temperature of austenite by certain combinations of alloying elements and rates of cooling, to a temperature range within which the face-centered cubic space lattice of austenite can change to the body-centered cubic space lattice of ferrite independently of the iron carbide formation. While the mechanism of this change from austenite to martensite is very imperfectly understood, it seems probable that the transformation begins from many centers and the main change occurs by the progressive growth of the ferrite from these many centers. The austenite would of course decompose at the surfaces of the ferrite grains. Only a slight shift in the atoms is required to produce this change. The carbon would be largely trapped in substantially the same distribution in which it existed in the austenite. The carbon atoms can diffuse slowly at room temperature and more rapidly at higher temperatures. A small amount of iron carbide could form simultaneously with the austenite transformation. The rate of diffusion of the carbon is so slow that the carbide formation is not completed except after very long aging at room temperature, the time becoming shorter the higher the temperature.

3. I believe that such carbon as remains in atomic dispersion in the ferrite is probably in between the space lattice points. I do not believe that Fe_3C is in solid solution in the ferrite.

4. I believe internal strains play an important part in the *hardening* of steel chiefly because of the volume changes accompanying the transformations; i.e., strains determine in part to what extent the main transformation takes place. I do not believe that internal strains have any important direct bearing on the *hardness* of steel. If there is any effect, internal strains would probably decrease rather than increase hardness.

H. LE CHATELIER†

1. The hardness of martensite is a specific property of that solid solution similar to the hardness of bronze containing 20 per cent. of tin. I do not know of any

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previous observation by which this hardness can be explained. Solid solutions of zinc in copper are not hard while those of tin in copper are hard. Silicon is a soft substance but when it is combined with oxygen it yields a very hard substance. In the same way, when alpha iron dissolves carbon, it hardens, while gamma iron behaves differently. One must not try to explain everything.

2. In order to produce martensite the solid solution austenite which is stable at a high temperature must be cooled rapidly enough to a temperature at which separation of the carbide from the solid solution cannot take place, i.e., below 200° C. for ordinary carbon steel, and to a higher temperature for chromium and tungsten self-hardening steels. The temperature, however, should not be so low as to prevent the return of the gamma iron to the alpha stage. Cooling therefore must be rapid down to a temperature comprised between two limits depending upon the composition of the steels. Above this temperature zone pearlite is produced or some transition constituent such as troostite. Below that zone, austenitic steel results. This contains gamma iron and is non-magnetic.

3. I have no opinion in regard to the condition of the carbon in martensite. There is no experimental method by which the condition of substances in solution can be ascertained. In the case of salts dissolved in water as, for instance, sodium sulfate, some believe that it is the solid salt, others that it is a mixture of hydrates, and still others that the salt no longer exists, having been decomposed into ions. It is a question of sentiment. In this case, my sentiment is that carbon exists as cementite because it is under that form that it separates from its solution.

4. I have never studied the lattice structure of iron and have no opinion on that subject.

5. I do not believe that strains can play any role in the hardening of steel. When the stresses are uniformly applied to a metal in such a way as to prevent any deformation, no increase of hardness results, as this depends solely upon the extent of the deformations. Since the stresses which may occur when gamma iron changes to alpha are not accompanied by deformation, they cannot be a cause of hardness.

H. H. LESTER*

1. It seems to me that martensite may be defined as an aggregate of small distorted iron crystals, which crystals may represent a solid solution of iron and carbon. The crystals are usually those of alpha iron, but gamma iron crystals may be present and may even preponderate in rare cases. Carbon atoms or other foreign atoms seem to be essential. Their presence in the iron crystals serve to distort those crystals and probably serve also to retard crystal growth. The hardness of martensite seems to me to be due to the combined effects of small crystal size and warped crystal planes in preventing slip along atomic planes.

2. Conditions necessary for the formation of martensite are the presence of foreign atoms in excess of the amount that would form an unsaturated solution with the iron at ordinary temperatures and a rapid cooling rate from a point where the foreign atoms are held in unsaturated solution to a point where the solution would be supersaturated. Conditions that are peculiarly helpful and that are present naturally where martensite is formed with the presence of carbon are the presence of an allotropic transition point and a higher solubility for carbon in the allotropic form corresponding to the higher temperature. Martensite is then formed by a rapid cooling through the gamma-alpha transition point. The mechanism of formation consists essentially in the formation of a supersaturated solid solution. The crystals of the solution are small, but not necessarily smaller than a critical size that permits the obtaining of sharply defined x-ray crystal spectrum lines.

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3. I regard the martensite with which most of us are familiar to be a solid solution. I think that the carbon atoms occupy positions near to, but not necessarily on lattice points of the alpha iron crystals. It seems probable that each carbon atom may be associated with three adjacent iron atoms, the four atoms replacing four iron atoms and occupying positions near to, but not on lattice points of the alpha iron crystals and forming in effect a molecule of iron carbide. From this view we obtain that the solution is a molecular dispersion of iron carbide in alpha iron, and differs but little from an atomic solution of carbon in alpha iron.

4. If strains be taken as displacements of atoms from positions of stability then strains within the crystals may be regarded as one of the two principal factors in the hardening of steel, the other being the smallness of the crystals. In this the strains measure the distortion within the crystals; the distortion and not the strain may be regarded as the primary cause of the hardness.

FRANCIS F. LUCAS*

1. In my opinion martensite is a decomposition of austenite along the octahedral crystallographic planes. That martensite is not a solid solution seems to be true because more than one constituent is visible under high magnification. Martensite responds strongly to two dissimilar etching reagents, picric acid and boiling sodium picrate, one of which etches ferrite readily but does not attack iron carbide and the other which stains iron carbide but does not etch or stain ferrite. Neither reagent seems to have appreciable effect on austenite under the same etching conditions. The sodium picrate usually stains austenite a straw yellow.

The particle size of the ferrite and the carbide constituents present in martensite seems to be bordering just on the range of present microscopic vision and it is possible that these particles either singly or in groups may be resolved by methods yielding a higher degree of resolution than heretofore employed.

The conclusion seems justified that iron carbide must be present in martensite and it is my opinion that the iron is probably present in the alpha state. The carbide must be present in a highly dispersed condition. The uniformity of the structure of martensite indicates a regular and an orderly procedure in its formation. Deep etching does not develop etching pits but does bring out either a mottled appearance or a mother-of-pearl coloration. When this coloration is present the structure is found to be laminated. The lamellae are continuations of the crystallographic planes inherent in the austenite. Multiple twinning frequently is found to occur in martensite along these crystallographic planes.

No evidence has been found that a plain carbon steel may become fully martensitic. The structures at high powers are seen to consist of austenite and martensite but more often of austenite, martensite and troostite, sometimes of even lower orders of decomposition.

Martensitic needles have never been found to cross grain boundaries or twinning planes, *i.e.*, each needle is contained within a zone of uniformly oriented austenite.

Each needle has a midrib or vein which etches more deeply with picric acid than does the rest of the needle. The presence of a midrib in the martensitic needle seems first to have been discovered by Osmond. It is almost always a straight line and in my opinion marks the path in the crystallographic plane along which decomposition from austenite to martensite first took place, *i.e.*, it is the first metal transformed. Since decomposition to lower orders is progressive unless arrested, these midribs or veins, in my opinion, indicate that the first transformed material has had time enough during the quenching to undergo secondary transformation form-

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ing troostite so that the midribs of the martensitic needles when they appear are really troostite and the outer parts of the needle are martensite.

In my opinion the hardness of martensite is due to the presence of iron carbide in a highly dispersed condition.

2. In my opinion the evidence to date seems to indicate that martensite is formed at a high temperature rather than at a low temperature. Drastically quenching an iron carbon alloy (C. 2.65 per cent.) results in austenitic grains containing a few needles of martensite—no other constituents are present in the grains selected which can be recognized under the highest powers of the microscope. Tempering at 200° C. for a long time does not result in the development of more needles within the grains. It does cause the needles to decompose in part or in their entirety to troostite. The austenite also undergoes some decomposition of a troostitic nature. The microscopic evidence seems to indicate that if a given iron carbon alloy is quenched drastically the martensitic needles are feather-like acicular needles, *i.e.*, more perfectly formed, and less troostite is present. If quenched from a lower temperature in a less drastic manner than in an ice and brine solution, the martensitic needles are not long, tapering and well-formed, but are quite broad and of rather indistinct outline. The structure also contains much troostite in small particles. It seems to me that martensite is formed by the first shock of quenching.

3. I do not believe martensite to be a solid solution.

4. Practically an unimportant one. Strains, in my opinion, are an effect of hardening rather than a cause.

JOHN A. MATHEWS*

I consider martensite as a solid solution, but whether of carbon or carbide I am not yet certain. There seems to be two ways by which martensite could be produced. One by quenching from a temperature above the critical and the other by cold work. During the quenching operation most of the austenite is converted to martensite, if not all. In the case of cold work on austenitic steels, it has been shown that the austenite is directly converted into martensite under stress. Therefore it seems to me that in addition to Jeffries' theory, stress does play some part but not a prominent part.

A. McCANCE†

1. Martensite, in my opinion, is an enforced solution of carbon in a mixture of alpha iron and gamma iron, but in which the alpha iron is largely predominating. On quenching there is a critical rate of cooling which varies with the composition of the steel and allows the change from gamma iron to alpha iron to take place, but does not permit of the carbon coming out of solution. Consequently, the normal alpha iron space lattice is distorted, owing to the presence of the carbon atoms, and the hardness of martensite is a consequence of this state of distortion.

2. The conditions necessary for its formation are the presence of carbon in solution in a region of temperature where gamma iron is stable, and a rate of cooling from this state to normal temperatures which exceed the critical rate of cooling explained above.

3. I believe that the carbon atoms exist at the center of unit cubes of eight iron atoms and replace the center iron atom in the normal alpha iron lattice.

4. Strains take no part in the hardening of steel.

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BRADLEY STOUGHTON*

I believe that martensite is the first stage in the decomposition of austenite, and that the bulk of the evidence indicates that it is the beginning of a decomposition of the solid solution of carbon and gamma iron. I believe that its hardness is caused by internal stresses within the crystal which prevent intracrystalline slippage.

I take it for granted that the conditions necessary for the formation of martensite are the cooling of austenite through the range of its normal decomposition at a rate so rapid that complete decomposition cannot occur, but yet not quite rapid enough to prevent any decomposition. It seems to me that the mechanism of the partial decomposition must consist in a change from gamma iron to alpha iron and a separation of this alpha iron from solution. I do not know any evidence as to whether the change from gamma to alpha precedes the separation from solution, but I should assume that the change from gamma iron to alpha iron would be the first step in the decomposition, both because there would be no tendency to separate from solution unless the iron were changing into the alpha state, and second because the change from gamma to alpha is evidently a much more rapid one than the separation of iron from solid solution, as evidenced by the fact that cooling is not rapid enough to bring pure gamma iron to atmospheric temperatures, but it is comparatively easy to bring a proportion of solution to atmospheric temperatures by rapid cooling.

You ask whether I believe that the solid solution is of iron with carbon, or of iron with cementite. I have no opinion on this question and have used the general term of iron with carbon, without intending to indicate thereby any prejudice against a belief in a solid solution of iron with cementite.

I believe, in a general way, in the evidence given by the x-ray spectrometer, but I can not agree that the results can be interpreted with sufficient definiteness and accuracy to indicate what positions the atoms of the different elements occupy in the space lattice. It seems to me that the x-ray spectrometists overlook the complicated nature of the atom as indicated in the electron theory of matter.

I believe that strains existing in the interatomic bonds within the space lattices are chiefly responsible for the inflexibility which I associate with the hardness of steel. I believe that the bonds are under such stress that they have not the elasticity to permit deformation without rupture. The slip interference theory for the hardness of overstrained metals seems to meet that particular type of hardness only to a limited extent.

F. C. THOMPSON†

1. Martensite is a supersaturated solid solution of carbon and iron carbide in alpha iron, together with, under normal conditions, a certain amount, probably small, of unchanged austenite. It is not uniform in composition, the needles being of different carbon content from the rest of the mass. They are probably lower in carbon than the matrix. It is formed by needles of alpha iron containing carbon forming from the austenite under the action of the stresses set up in the process of quenching. These needles are not twinned gamma iron but are probably to some extent pseudomorphic after the latter. The hardness is due to several factors. In the first place the needles formed act as strengthening scaffolds throughout the mass. Secondly, there must be an appreciable amount of distortion of the space lattices which will also increase the hardness. And, finally, I do not see how there can but be severe internal stresses which will also have the same effect.

Even where needles cannot be seen I still think that they are present, perhaps on an ultra-microscopic scale. The law of mass action appears to me to demand that

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both free carbon and iron carbide should be present in solution. The tempering properties also seem to me to be compatible only with the view that some austenite, or perhaps more strictly speaking gamma iron, is normally retained.

2. The conditions necessary for its formation appear to me to be limited to the single condition that the rate of cooling should be greater than a certain critical value. The mechanism of the formation is the gradual production of needles of a supersaturated solution of carbon and carbide in alpha iron along the octahedral planes of the original austenite. These are of lower carbon content than the original austenite, which latter must, therefore, become richer in carbon as the process proceeds. The volume change due to the change from gamma to alpha iron will cause internal stresses and strains of a gradually increasing magnitude.

3. All that I think can be definitely said at the moment is that the carbon atoms rest in between the iron atoms.

4. Already answered. Hardening cracks are the best evidence for the existence of very severe internal stresses approximating to the tensile strength of the material.

DISCUSSION

Z. JEFFRIES AND R. S. ARCHER, Cleveland, O. (written discussion).—The members of the Institute are indebted to Prof. Sauveur for his compilation of current opinion on the hardening of steel. Quite aside from any possible value in the establishment of scientific truth, such a digest can not but be interesting, and will probably be still more interesting in retrospect "thirty years later."

There is, of course, only one correct answer to the question, and it should be the object of all scientists to ascertain this answer. It is not anticipated that all the details of this problem will be worked out for many generations. It is important, however, in these studies to hold the ground which science has already won, to provide a sound foundation for further investigation, and to thus progress toward an even better understanding of the hardening and hardness of steel.

It seems probable that much ground would be lost if certain of the views put forward in the present paper were given the weight ordinarily accorded Prof. Sauveur's conclusions. His ideas on the sequence of changes in the hardening and tempering of steel, his conception of troostite, and his views on beta iron as a factor in hardening are at variance with the great mass of existing evidence. In fact, he makes no attempt to reconcile his views with the conflicting evidence.

The writers were interested in Prof. Sauveur's "clear anticipation" of the slip-interference theory of hardening, as stated in his paper. (See page 874.) In preparing their statement of this theory⁶ the writers availed themselves of the results of many previous investigations, the most fundamentally important of which were carried out within the last 30 years. If there is any merit in this statement, the credit is due to the entire body

⁶ Zay Jeffries and R. S. Archer: Slip-interference Theory of the Hardening of Metals, *Chem. and Met. Eng.* (June, 1921).

of scientific men whose work has made the generalization possible. The establishment of truth is, however, a more important objective than the apportionment of credit.

It is not desired to detract in any way from Prof. Sauveur's splendid pioneer work on the hardening of steel, but the writers would like to point out that, his theory of hardening of 1896 as given on page 874, is not in accordance with their own. The slip interference theory in part rests on the following fundamental postulates:

1. The hardness and strength of even the hardest alloys depend primarily on the high inherent cohesion of the atoms of the predominant metal.

2. Metals are commonly soft because of the existence of planes of potential slip which render impossible the realization of this inherently great cohesion.

3. The hardening and strengthening of metals by any of the known methods may be considered as due principally to "slip-interference."

Prof. Sauveur's explanation of 1896 involves the older conception that iron is inherently soft, so that the hardness of hardened steel must be due to the presence of some material which is itself very hard. In fact, he supposed that it was necessary for the soft iron to be surrounded "on all sides" by the hard cementite. There was naturally no mention of the fundamentally important slip mechanism of deformation, since this was not discovered until after 1896.

The problem of the hardness of hardened steel is now one of evaluating the various factors which may increase resistance to slip. This evaluation must rest, of course, on a true conception of the constitution of hardened steel.

During the last few years considerable progress has been made in quantitative estimates of the slip-resisting factors in both ferrous and non-ferrous metals and alloys. At the present rate of progress a still better understanding of hardened steel can confidently be expected in the near future. The writers can hardly agree with Prof. Sauveur that the progress of the last 30 years "does not constitute a very material advance if advance at all."

S. L. HOYT, Schenectady, N. Y.—I should like to associate with Dr. Jeffries and Mr. Archer in expressing appreciation of this contribution of Prof. Sauveur, but time is limited and I will proceed to a few remarks.

I notice that Prof. Sauveur lays emphasis on the phase rule and its requirement as applied to the study of the constitution of steel. In that connection I would interpret Prof. Sauveur's paper as assuming four phases to be in equilibrium at the pearlite transformation point; the first being austenite; the second, troostite; the third being iron of the pearlite, and the fourth iron carbide of the pearlite. But the phase rule shows that four phases are not possible under conditions of stable equilibrium.

Prof. Sauveur indicates in his diagram that they do not occur simultaneously, but if we have stable equilibrium, the phases present during equilibrium must co-exist. I would like to hear if Prof. Sauveur feels that separating these phases in the diagram eliminates the disagreement with the requirements of the phase rule.

We also have further evidence which to my mind shows that these phase relationships are different from what Prof. Sauveur assumes: Firstly, pearlite has been shown by Col. Belaiew to form on octahedral planes of a face-centered cubic lattice. According to Prof. Sauveur's description, pearlite would form in a body-centered lattice. Secondly, pearlite which forms from troostite, is known to be granular pearlite, but the pearlite which forms on slow cooling is lamellar pearlite. Consequently, these two experimental facts are opposed to the conception Prof. Sauveur has presented.

The general disagreement among metallurgists to whom the paper was submitted indicates that something rather fundamental is still lacking and as if we did not have the proper fundamental conception of the constitution of quenched steel.

Last fall in Cleveland I had the pleasure of reading a paper by Hanemann and Schrader which dealt with the subject and presented an entirely new viewpoint. Since reading that paper, the metallurgical colloquium at the Research Laboratory has made a study of the paper, and it appears to us to be inherently sound, and offering a very valuable viewpoint from which to consider the constitution of steel. This is to be published in the February number of the *Transactions* of the American Society for Steel Treating, and it seems to me that those interested in this question can study this paper with a great deal of interest and profit.

J. ALEXANDER, New York, N. Y. (written discussion).—Prof. Sauveur's paper is most welcome, not only to metallurgists, but also to those lesser breeds of scientists without the law of metallurgy who dare to look from their own angle at so highly a disputed question as that of the hardening of steel. His 1896 paper on this topic registered direct hits in two important particulars: 1, that fine dispersion is a vital factor in the hardness of martensite; 2, that the details of its structure are so minute, that even the highest magnification gives little indication of its chemical composition or structural character. (Parenthetically, I may observe that the colloidal zone begins just about at the limit of microscopical resolvability.)

Metallographs, like biological slides, even in what they do show, may often exhibit *artifacts* consequent on the treatment of the specimen; but in any event, they fail to reveal the important submicroscopic structure of the material involved. The *x*-ray spectrometer, in jumping from dimensions measured in microns to those measured in Angstrom units, leaps over the colloidal zone lying between; and while it can tell us much

about the space lattice of crystals, is not determinative of the *size or distribution of sizes* of the very crystals into whose inner structure it prys.

THE ZONE OF MAXIMUM COLLOIDALITY

Metallurgists are facing in their own field what chemists and physicists are still fighting over—the lines of demarcation between solution, colloidal solution and suspension. If we could but apply the ultramicroscope to metals, as has been done with solutions, colloidal solutions, suspensions and even solid soaps, glasses and pyrosols (Lorenz), much evidence now hidden would be brought to light. Just in this neglected area we have what I termed the zone of maximum colloidality, and what Merica and Jeffries and Archer called critical dispersion.

The fact that S. U. Pickering was able to make extremely stiff masses by the mayonnaise method of emulsifying finely soap water and kerosene, indicates that degree of dispersion with its tremendous release of surface forces, rather than “keying effect” is a critical factor in hardening; for soap water and kerosene can hardly act as keys. Similarly, the firmness of putties made by mixing a definite weight of oil with like weights of any inert mineral ground down to varying degrees of fineness, will increase in proportion to the fineness of the grinding—the zone of maximum colloidality, which approaches that of true solution, is not as a rule reached in this fashion.

Sweeping aside, as the shadow, all such apparent differences in answers to the questionnaire as are due to variations in nomenclature, scope of definition or confusion of effect with cause, and *visualizing the material phenomena beneath*, it seems to me that most of the metallurgists consulted believe that fineness of dispersion is a dominant factor in hardening.

A return to first principles might be aidful, since there is no reason to believe that metals are exempt from the general laws of nature. Therefore let us first consider the basic meaning of “hardness” and the methods whereby it is measured.

HARDNESS

Concisely, “hard” means not easily scratched; “hardness” means resistance to scratching, indentation, or abrasion. Hardness is usually determined by forcing, under pressure, against or across the object being tested, another hard object, and noting the nature of the scratch or dent, if any. Mineralogists use Moh’s table comparatively. This begins with talc and ends with diamond, the standard minerals being mainly definite chemical substances possessing a definite space lattice. Overlooking the differences between the different crystal faces of the same crystal, their hardness is due to the specific attractions of their constituent particles (atoms, molecules, or molecular groups, as the case may be).

In the case of sandstone, for instance, the particles are quite visible, and consist of millions of molecules.

When we leave the domain of chemical individuals, and study *aggregates*, the phenomena become more complex; for we must then consider the *interfacial* forces between the individual constituents, as well as the *intrafacial* forces within them. We have every reason to believe that the bond between two different interfaces may be stronger than that of either free surface to its own kind—just as a man may leave his parents and cleave to his wife. Thus a glued wooden joint is considered satisfactory if the wood splits before the glue lets go; in which case the interfacial forces glue/wood and glue/glue are greater than the forces wood/wood. With aggregates, as the free surfaces increase, their effects increase, until molecular subdivision is approached. Then the tendency of the particles toward assuming a space lattice relationship to each other, results in a decrease in hardness, a condition which might be considered as a straining toward a position of minimum of potential; for kinetically speaking, the deadest thing is one big crystal. (Would not "One Big Union" be the social counterpart?)

With colloids, whether they consist of ultramicroscopic crystals or random groups, quite the opposite is the case. As Thomas Graham remarked: "Colloids possess *Energeia*, which even in metals, may slowly express itself. Tin and lead anneal at room temperature, and old lead roofs are said to consist of a few large crystals. Freshly-deposited travertine at Mammoth Hot Springs (Yellowstone Park) is cryptocrystalline; but on going up the hill I found increasing evidence of crystallinity, until, at the top, where geologists estimate the deposits to be 20,000 to 30,000 years old, I found large glistening crystals."

THE INTERMEDIATE COLLOIDAL ZONE OF DISPERSION

To reach the state of microscopically-visible particles from a state of true molecular dispersion (which often occurs on cooling), or conversely, to reach a state of true molecular dispersion from visibly coarse subdivision (which often occurs on fusion), the melt *must* traverse the gauntlet of the intermediate colloidal zone of dispersion. This obvious principle has been experimentally demonstrated by von Weimarn, the well known Russian physical chemist. With metals and alloys, the transition may be complicated by intercurrent allotropism, chemical changes and variations in degree of solubility with temperature.

Metallurgists are not quite agreed upon the chemical identity of the individual phases or individual substances in martensite, but the preponderance of evidence is that we have there mainly a dispersion of cementite (Fe_3C) in the alpha allotrope of iron. When hardened steel is treated with acid, a large part of the carbon combines with the hydrogen incidentally formed, and comes off as hydrocarbon gases of peculiar

odor. This is not so with tempered steel, and is evidence of the extreme fineness of the cementite in martensite. As several point out, martensite may contain some free carbon and some gamma iron, for we have an attempt toward a kinetic equilibrium, which is interrupted by increase in viscosity, but which slowly strives to establish itself. Hence, as Prof. Sauveur puts it, fresh martensite begins to age as soon as it is formed. This aging is quite characteristic of colloidal dispersions, and is due to aggregation.

On reading over the views of the many distinguished metallurgists who answered the questionnaire, as well as Prof. Sauveur's own views, the fact emerges that many of them believe and practically state, though in other and various language, that martensite is essentially a colloidal dispersion of cementite in alpha iron. Only Grenet, however, comes out with this form of expression, which brings the phenomena involved in the hardening of steel into line with phenomena in many other fields of knowledge.

So far as I know, Dr. H. Kneebone Tompkins was the first to point out the analogy between colloidal and metallurgical phenomena. His thesis, presented in 1896, lay unknown in the archives of the University of London, until it was published as an appendix, in 1920, to the Report of the Joint Discussion on Colloids of the Faraday Society and the Physical Society. Prof. C. Benedicks (about 1907), Prof. Wolfgang Ostwald (about 1911), and no doubt others besides myself came independently to the same view. But the idea of the zone of maximum colloidality, which I advanced some time ago, seems to show why martensite is harder than the finer austenite or than the coarser troostite. [Besides *Journal* articles, see my "Colloid Chemistry," 2nd. ed., 1924, and "Colloid Chemistry, Theoretical and Applied," Vol. I, Ch. 1 (now in press).]

A. SAUVEUR (written reply to discussion).—Discussion of technical papers should be, I believe, confined to criticism of the evidences offered by the author in support of his views or to criticism of his argumentation. Those who have discussed my paper having failed to do this a reply is hardly necessary.

In regard to Dr. Hoyt's reference to the phase rule, I simply meant to call attention to the fact that if we accept the views generally held of the nature of martensite and troostite, then quenched steel frequently contains four phases; namely, the solid solution austenite, the solid solution martensite, the element iron and the compound Fe_3C , while accepting my conception of the nature of troostite but two phases are present; namely, the solid solution austenite and the solid solution troostite.

In referring to the views I tentatively expressed some 30 years ago to explain the hardening of steel, I had no desire to detract from the import-

ance of Dr. Jeffries' and Mr. Archer's contribution to the study of this question. My only reason for mentioning them was to support my contention that no considerable progress had been made in the last 30 years in our attempt to explain the hardening of steel. Notwithstanding Dr. Jeffries' and Mr. Archer's statement, I still believe that the views I then expressed were quite anticipatory of what they call the "slip interference theory." If those interested will take the trouble of reading my paper of 1896 they may judge for themselves.

Dr. Alexander's interesting remarks take us at least out of the beaten track into a field which he, at any rate, and some others consider full of promise. His philosophy and breadth of view are refreshing and I for one wish him and his co-workers Godspeed. Is there a colloidal world and does martensite belong to it?

In the realm of solids are colloids necessarily harder than the solid solutions which give them birth, and harder than the aggregates which they in turn beget? If martensite is a colloid it should be borne in mind that it differs from its parent in containing iron in the alpha condition whereas the former contains gamma iron. There is here a critical (allotropic) change accompanying the transformation of the solid solution into a colloid which is not generally observed. It is precisely why it is difficult to consider the hardening of steel merely as an instance of the well known greater hardness of solid solutions compared to that of the solvents, be this due to fineness of grains, to distorted lattices, to the greater attraction between foreign atoms, to dispersion of the solute or to other causes.

An Introduction to Ultra-violet Metallography

By FRANCIS F. LUCAS,* NEW YORK, N. Y.

(New York Meeting, February, 1926)

PREVIOUS WORK

A microscope objective of given numerical aperture, when used with light of given wave length, has some fixed limit of resolution. This may be expressed as potential resolving ability—the ability to resolve is inherent in the lens but whether this limit is achieved in practice is quite another matter.

Nearly 50 years ago Abbe evolved theoretical considerations which indicated that the ability of a lens to resolve detail is directly proportional to twice the numerical aperture of the objective and inversely proportional to the wave length of the light used. It is true, unquestionably, that as the numerical aperture of the objective is increased the potential resolving ability of the lens is increased and likewise when the wave length of the light used is decreased, the degree of resolution is increased. Whether Abbe's formula expresses the exact relationship is not a matter of great concern. It suffices to know that to improve resolution, other things being equal, two avenues of approach are available. Either the numerical aperture of the objective may be increased or the wave length of the light decreased. With the apochromatic system it is possible to employ successfully wave lengths from 400 to 500 $\mu\mu$ and still secure reasonably short exposures. The present limit for numerical aperture is 1.40 N. A. although objectives of 1.60 N. A. are now an experimental possibility for metallurgical work. Thus certain well defined limits are set for those who work within the range of the visible spectrum.

In order to take advantage of the increase in resolving power which accompanies a decrease in the wave length of light employed, Dr. A. Köhler and Dr. M. Von Rohr of the Zeiss Scientific Staff developed the "monochromats." These are quartz objectives corrected for the single wave length 275 $\mu\mu$ which lies in the ultra-violet region of the spectrum. They also developed a series of quartz oculars and a complete photomicrographic equipment with which to use the quartz optics. Quartz must be used for the optical parts because glass absorbs ultra-violet light almost completely. Thus there was made available about 20 years

* Bell Telephone Laboratories, Incorporated.

ago a complete photomicrographic equipment capable of working in the ultra-violet range. This equipment was intended primarily for transparent specimens mounted on quartz slides and covered with quartz cover glasses. It seems that at least several equipments were manufactured which also were intended to be used for metallurgical work. An exhaustive search of the literature has not been made, but the records appear to contain little information of results achieved.

About 4 years ago, in order to investigate the possibilities of ultra-violet metallography, the Bell Telephone Laboratories arranged with the Zeiss Scientific Staff to design a complete photomicrographic equipment using a wave length of $275\mu\mu$. It was desired to obtain if possible a horizontal type of equipment similar in design to the Martens metallurgical outfit, which had been used successfully at high powers. The design of such a horizontal type of equipment was deemed impracticable by the Zeiss Staff so that the equipment finally developed was of the conventional vertical type.

DESCRIPTION OF APPARATUS

In this equipment the source of illumination is a spark gap and a quartz slit. The light passes through a collimator and two prisms of

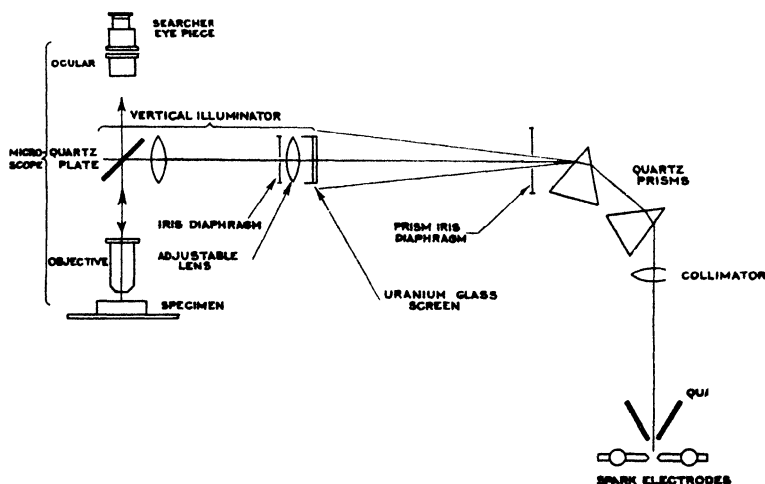


FIG. 1.—SCHEMATIC DIAGRAM OF OPTICAL SYSTEM FOR WORKING IN THE ULTRA-VIOLET RANGE.

quartz to emerge from the prism diaphragm in the form of a line spectrum. The desired line is focused on the vertical illuminator of a metallurgical microscope and, by means of a suitable optical system contained within the vertical illuminator, is caused to illuminate a quartz plate which deflects the light downward to the specimen as in any metallurgical microscope using the Beck type illuminator. Since light waves invisible to the

human eye are used, a fluorescent screen is employed to center the light on the aperture of the vertical illuminator. Once the light is centered this screen is removed and another is substituted in the form of a searcher eyepiece. The searcher eyepiece is used to view the image and it is placed just above the ocular of the microscope. A schematic diagram of the optical system is shown in Fig. 1.

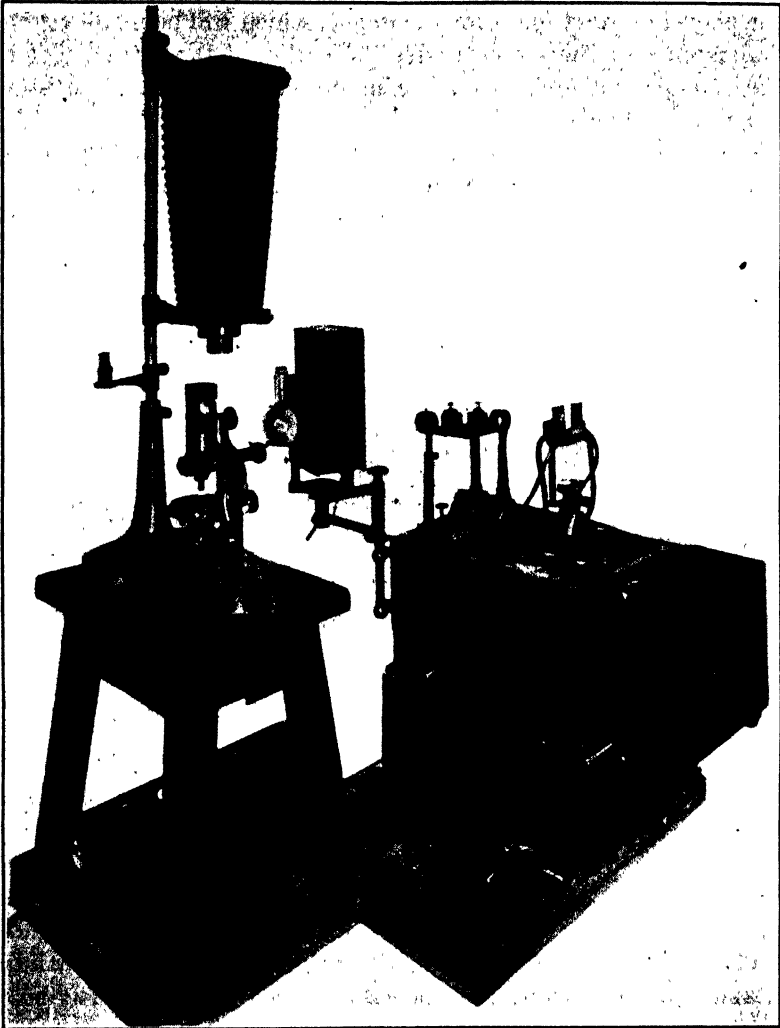


FIG. 2.—EQUIPMENT USED IN ULTRA-VIOLET PHOTOMICROGRAPHY.

The assembled equipment (Fig. 2) consists of two units. The microscope is the research stand fitted with a special vertical illuminator. It is secured to the base of the vertical camera stand. The camera is for 5 by 7-in.

plates, or smaller, and permits a bellows extension of 80 cm. but an extension of approximately 30 cm. only is used because of the focal computations which enter into the problem. The camera is arranged to swing out of position so that a searcher or focusing eyepiece, may be brought into position just above the ocular of the microscope.

The searcher consists of a fluorescent screen which is viewed by a magnifier. The fluorescent screen has cross rulings so that the magnifier may be placed in exact focus for the image, which will be made visible by the fluorescence of the screen under the action of the ultra-violet rays.

The camera and microscope are mounted on a stool of substantial construction as shown.

The vertical illuminator consists of a quartz plate mounted in a tube and capable of being accurately adjusted. The illuminator has its own optical system including a diaphragm which must be coordinated with the illuminating train of the spark-generating equipment. The illuminator is illustrated in Fig. 3.

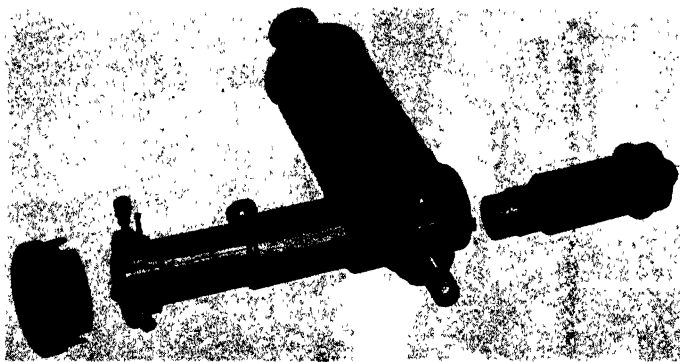


FIG. 3.—ILLUMINATOR USED WITH EQUIPMENT SHOWN IN FIG. 2.

The spark generating equipment is mounted in a case which is spaced 32 cm. from the microscope stool. It consists of a wooden cabinet supported on a box to match. Two condensers and a safety spark-gap are mounted in the bottom of the cabinet. On top is a T-shaped, adjustable optical bench carrying a diaphragm, a prism table, a collimator and the spark stand. The electrode terminals have a micrometer screw adjustment and both electrodes are opened or closed simultaneously so that the gap will function centrally before a quartz slit mounted on the frame of the spark stand. The electrodes are strips of cadmium or magnesium.

Mounted on the end of the cabinet is a small mercury vapor lamp in a suitable metal housing. The flask mounted in front of the opening in the lamp housing, is filled with a green filter solution yielding approxi-

mately monochromatic light and is used as a condenser. This lamp assembly may be used in two ways. Either it may be swung around between the two units of the equipment and thus illuminate the vertical illuminator directly or it may be swung back so that a small mirror reflects the light through the prism diaphragm. By this latter arrangement it is possible to center the illumination with the mercury vapor light by aligning the optical system of the microscope with reference to the aperture of the prism diaphragm.

The mercury vapor lamp has another important function to perform. It provides a steady source of approximately monochromatic illumination, free from noise, by which the operator can focus the specimen, study its structure, and select a field as a preparatory step to photography with the ultra-violet illumination. Once the field is selected with the mercury vapor light, it must be refocused with the ultra-violet light using the

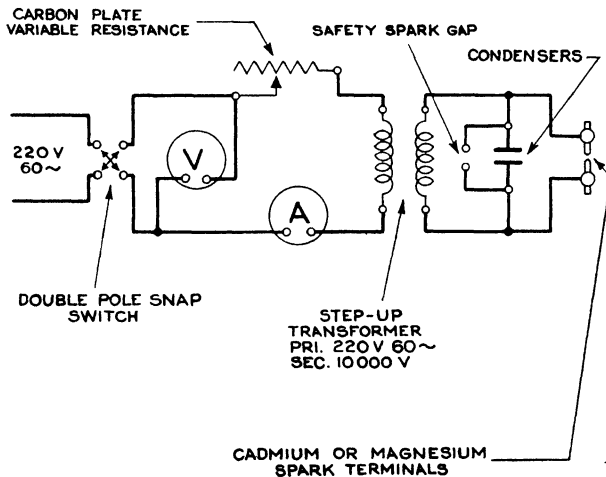


FIG. 4.—DIAGRAM OF ELECTRICAL SYSTEM WITH EQUIPMENT SHOWN IN FIG. 2.

searcher eyepiece. This is necessary because the effective rays of the mercury vapor lamp lie within the visible spectrum. For ultra-violet photography the image must be focused with the line used, either the cadmium or the magnesium line as the case may be.

The spark is generated by a step-up transformer, the output of which is regulated by a carbon plate rheostat in the primary winding. When the system is functioning properly the primary current is 2.5 to 3. amp. at a voltage of 220 and a frequency of 60 cycles. The secondary potential is 10,000 volts. Fig. 4 gives details of the electrical system.

An expanded metal cage lined with amber glass affords a maximum degree of protection for the eyes against the injurious action of ultra-violet light. This cage fits over the spark stand and has a hand hole for

access to the electrode-adjusting screw, also an aperture for the light to emerge to the collimator. This arrangement muffles the noise of the spark somewhat.

Tables 1 and 2 contain data compiled by the Zeiss company, descriptive of the monochromat objectives and the quartz eyepieces. The column of Table 1 headed "Relative Resolving Power" gives the equivalent aperture of corresponding objectives working with daylight, assuming such objectives were available. That is, the 6-mm. monochromat has an aperture of 0.35, but because of the effectiveness of the short wave length of light used, it develops resolution equivalent to that which would be developed by an objective of 0.70 N.A. when used with daylight.

TABLE 1.—*Monochromatic Objectives*
Corrected for $\lambda = 275 \mu\mu$ and 160-mm. Tube Length

SYSTEM	DESCRIPTION	RELATIVE RESOLVING POWER
Dry series.....	6 mm. num. ap. 0.35	0.70
Glycerine.....	2.5 mm. num. ap. 0.85	1.70
Immersion.....	1.7 mm. num. ap. 1.25	2.50

TABLE 2.—*Quartz Eye-pieces*

DESCRIPTIVE No.	MAGNIFICATION	FOCUS, MM
5	5	36
7	7	26
10	10	18
14	14	13
20	20	9

TABLE 3.—*Magnifications and Optical Camera Lengths, for the Monochromats and the Quartz Eyepieces at 160-mm. Tube Length and $\lambda = 275 \mu\mu$ Wave Length*

Objectives	Eyepieces	5	7	10	14	20
6 mm. NUM. AP. 0.35 R.R.P. 0.70	Magnifications . . .	200	300	450	600	900
	Optical camera-lengths	24 cm.	25.5 cm	27 cm.	25.5 cm.	27 cm.
2.5 mm. NUM. AP. 0.85 R.R.P. 1.70	Magnifications	250	400	500	800	1000
	Optical camera-lengths.	30 cm.	34 cm.	30 cm.	34 cm.	30 cm.
1.7 mm. NUM. AP. 1.25 R.R.P. 2.50	Magnifications	500	700	1000	1400	2000
	Optical camera-lengths . .	26.5 cm.	26.5 cm.	26.5 cm.	26.5 cm.	26.5 cm.
	Magnifications	600	800	1200	1600	2400
	Optical camera-lengths . .	31.5 cm.	30 cm.	31.5 cm.	30 cm.	31.5 cm.
	Magnifications	700	1000	1500	2000	3000
	Optical camera-lengths . .	24 cm.	24.5 cm.	26 cm.	24.5 cm.	26 cm.
	Magnifications	900	1300	1800	2500	3600
	Optical camera-lengths . .	31 cm.	32 cm.	31 cm.	31 cm.	31 cm.

The 2.5-mm. and the 1.7-mm. objectives develop corresponding improvements in resolving ability. The values given are theoretical and from the writer's actual observations appear exceedingly conservative. In fact it seems doubtful whether the possibilities of these objectives have been explored more than superficially so far as practical application is concerned.

EXACT FOCUSING

The ultra-violet microscope is an instrument of far greater precision than any other microscopic apparatus available for metallography. It requires great exactness of focus, which must be obtained by viewing an image on a fluorescent screen under an intensity of illumination that is in no wise comparable to that obtainable when working with the ordinary metallurgical equipments. In fact, the details of the image are just barely visible and some expedient must be employed to insure exact focusing, as will be described later. It does not permit sitting comfortably at a focusing screen and studying the minute detail of the image with a magnifier and making the exact focus which will accentuate the one characteristic of the structure which it is desired to portray. One must visualize the entire field and gage the state of focus by means of the small searcher eyepiece. The intensity of the illumination is hardly sufficient to do otherwise although the writer has experimented with various fluorescent screens in place of the usual focusing screen of the camera. He has concluded that the searcher eyepiece method is the most hopeful.

It became evident that if exact focus is to be obtained, except by chance, some method must be used to enable the operator to judge when the field is in focus other than by judging the details of the structure itself. Several methods were tried such as depositing fluorescent materials on the surface of the specimen, or lightly scratching the surface with a delicate instrument but the results were not satisfactory. The depth of penetration of the objectives seemed insufficient to insure exact focusing by the scratch method and the fluorescent materials tried appeared very coarse. By chance it was observed that carbon completely absorbed ultra-violet light and so it seemed likely that if finely divided carbon could be applied to the surface of the specimen then sufficient contrast would result between the carbon and the specimen to enable one to focus the border line exactly. The problem was to get the carbon applied as a thin layer in the form of a line and to have it adhere when the immersion objectives are used. This was finally solved in a very simple way. An ordinary piece of typewriter carbon paper is laid face down over the surface of the specimen and a line drawn with a single stroke of a sharp medium-hard drawing pencil. The line of carbon on the specimen can be quickly located; insures exact focusing and the carbon sticks regardless of the immersion fluid. This method has been used in connection with the pictures reproduced.

It will be observed that the illuminating train is in two units: that is, the vertical illuminator is not mounted on the same unit with the spark stand. This means that the beam of light emerging from the diaphragm on the small optical bench must be made to coincide exactly with the optical axis of the vertical illuminator. To accomplish this both units should be level and the barrel of the microscope then raised or lowered until the image of the spark registers in the center of a uranium glass screen, placed over the end of the vertical illuminator. The uranium glass screen, which fluoresces under ultra-violet light, is fitted in a cap that slips over the end of the vertical illuminator. The image of the spark is focused by means of the collimating lens on the optical bench.

The light from the spark as it passes through the prisms and the prism diaphragm is spread out in the form of a line spectrum and the line desired is brought to bear on the uranium glass screen placed over the end of the vertical illuminator for the purpose, by shifting the line-up of the optical bench. This bench is in T-form and is supported by three leveling screws, one of which functions with a bevel drilling in a plate and thus is restrained from moving laterally. The points of the other leveling screws bear on plates so that the optical bench may be shifted through an arc of 10 or 15° about the fixed screw which is the one next to the prism diaphragm.

With the optical system properly adjusted the image of the prism diaphragm cuts in on the field and is quite sharply in focus. It must be brought into axial alignment by means of the centering screws controlling the adjustable lens of the illuminator. The diaphragm of the illuminator does not cut in on the field and its function is similar to that of the diaphragm on the conventional Beck illuminator of which the ultra-violet illuminator is a modification.

For purposes of centering and aligning the equipment an achromat objective of low power is used in conjunction with a low-power Huyghenian eyepiece. These operations are carried out by means of the mercury vapor light, but as a final check the writer uses the ultra-violet light and the searcher eyepiece.

The objectives are provided with sliding objective changers so that once they have been centered with their respective sliders no further attention is required.

MAGNESIUM VS. CADMIUM SPARK

The writer understands that the ultra-violet equipment was originally designed for use with magnesium line $280\mu\mu$ but that on trial distinct images were not obtained. It developed that the magnesium line on careful analysis consisted of two lines very close together and it was thought a double image resulted for this reason. This led to the selection of the cadmium line, $275\mu\mu$, but unfortunately the intensity of this

line is far less than the magnesium line. Because of the brightness of the magnesium line one is sorely tempted to use it. So far as the writer is concerned he seems to have obtained crisp brilliant images with either the magnesium line or the cadmium line, nevertheless he withholds final judgment. One thing can be said for the cadmium spark—what it lacks in intensity of illumination it makes up for in noise and it quite outdoes the magnesium spark in this respect.

POSSIBLE OPTICAL COMBINATIONS

The optical combinations possible with the equipment and the magnifications obtainable are given in Table 3. This table is also from data

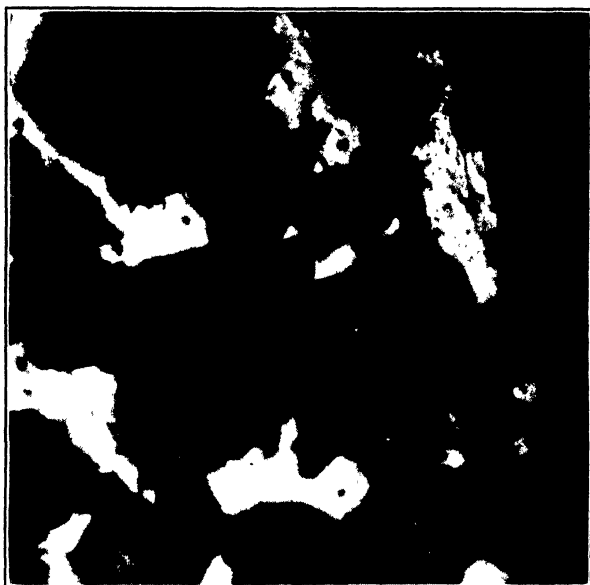


FIG. 5.—A TYPICAL ULTRA-VIOLET PHOTOMICROGRAPH "FLAT" AND "MUDDY." THE ILLUMINATION IS CRITICAL BUT THE IMAGE IS JUST OUT OF FOCUS. CRISP BRILLIANT IMAGES ARE NOT ATTAINED UNLESS THE FOCUS IS EXACT. THE SPECIMEN WAS A 0.50 PER CENT. CARBON COMMERCIAL STEEL HARDENED. THE BLACK AREAS INDICATING ABSORPTION OF LIGHT ARE TROOSTITE. TAKEN WITH 2.5-MM. OBJECTIVE AND 14 \times OCULAR WITH CADMIUM SPARK. THE MAGNIFICATION IS 1600 \times .

compiled by the Zeiss Scientific Staff. The equipment is so designed that when the image is sharply in focus in the searcher it will also be sharply in focus on the plate when the camera is set so that the plate will be about 30 cm. above the eyepiece. Apparently a few centimeters one way or the other in the position of the plate matters little and so the table is laid out, with two exceptions, to give magnifications in multiples of 100 \times . The time required for exposure will be doubled roughly, as the change from one to the next higher eyepiece is made.

The computation of the optical parts is so well balanced that the image appears to depreciate little if at all even when the highest power of eyepiece is used.

PLATES

The matter of suitable plates for ultra-violet work required much careful study. The difficulty seems to be to get a fine grained plate that is sensitive to ultra-violet light. The writer has used Wellington Anti screen; Eastman 40; Eastman 33; Hammer Ultra Rapid Blue Label and Hammer Special Red Label with about equal success. The characteristics of these plates are not all that could be desired and in some the grain is quite coarse.

RESULTS

At this time it is not the object to show the application of the ultra-violet microscope to the study of structures apparently irresolvable by

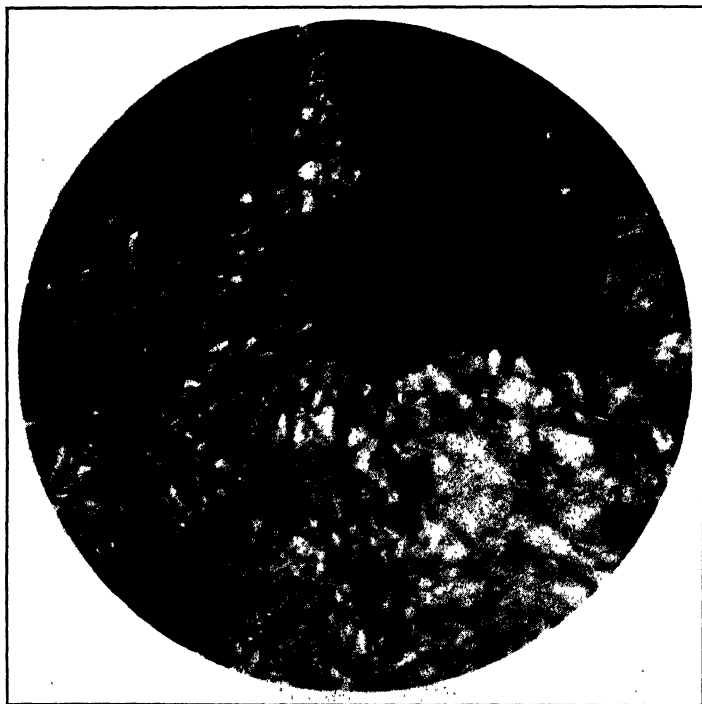


FIG. 6.—ILLUSTRATING LACK OF CRITICAL ILLUMINATION. THE CENTER OF ILLUMINATION IS NOT CONCENTRIC WITH THE OPTICAL AXIS. THE SPECIMEN APPEARS TO BE OUT OF LEVEL BUT ACTUALLY THE LIGHT IS AT FAULT. THE SPECIMEN WAS A HIGH-CARBON STEEL, HARDENED. NOTE ABSORPTION OF LIGHT BY THE TROOSTITE, WHICH IS REPRESENTED BY THE BLACK AREAS. TAKEN WITH 2.5-MM. OBJECTIVE AND 14 X OCULAR WITH CADMIUM SPARK. THE MAGNIFICATION IS 1600 X.

other methods, but to describe the equipment and to illustrate the results obtained when photographing well known structures. In this way the quality of the image may be judged and compared with results obtained with the apochromatic system.

Photographs taken with this equipment are shown in Figs. 5 to 15. The results obtained with ultra-violet light have usually tended toward "flat," "muddy" negatives showing little contrast and no brilliancy. The writer experienced this same sort of difficulty, but found that the trouble was due to one of two conditions or to a combination of the two: Either the image was not in exact focus or the illumination was not critical.

When the illumination is critical and the image is in exact focus the result surpasses by far the best results obtainable with the apochromatic system. For instance, a 16-mm. apochromatic objective has a numerical aperture of 0.30. This objective has little potential resolving ability. The 6-mm. dry series monochromat has a numerical aperture of only 0.35

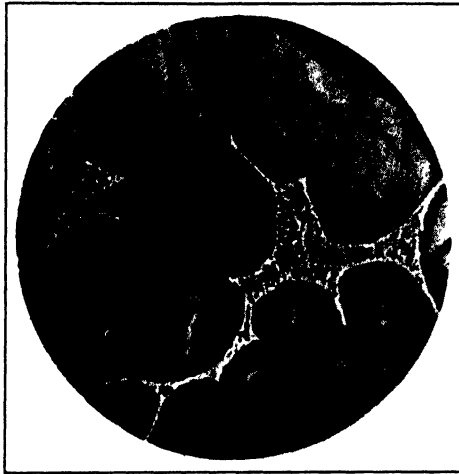


FIG. 7.—A SPECIAL HIGH CARBON-STEEL. NOTE THAT SOME OF THE MARTENSITIC NEEDLES ARE LIGHT AND OTHERS DARK INDICATING GREATER REFLECTION OF THE LIGHT BY THE FORMER. ALSO NOTE DARK SHADED ZONE BORDERING THE AUSTENITIC GRAINS. THIS ALSO IS INTERPRETED TO MEAN SELECTIVE ABSORPTION OF ULTRA-VIOLET LIGHT. TAKEN WITH 6-MM. OBJECTIVE AND 5 \times OCULAR WITH MAGNESIUM SPARK. MAGNIFICATION 375 \times .

but because of the effectiveness of the short wave length of light with which it is used, the potential resolving ability of the objective becomes equivalent, theoretically, to that of an apochromat of 0.70 N.A. Observations indicate that this is a very conservative estimate as the objective seems to have very nearly the same potential resolving ability as the objectives of 1.40 N.A. of the apochromatic system. The writer has observed that the monochromats produce a sharpness of detail which seems unattainable with the apochromatic system. This perhaps is one of the outstanding achievements of which the equipment is capable—the terms resolution and sharpness being somewhat synonymous. Without sharpness in the image resolution cannot be obtained and conversely if greater sharpness can be obtained then the resolution will be improved.

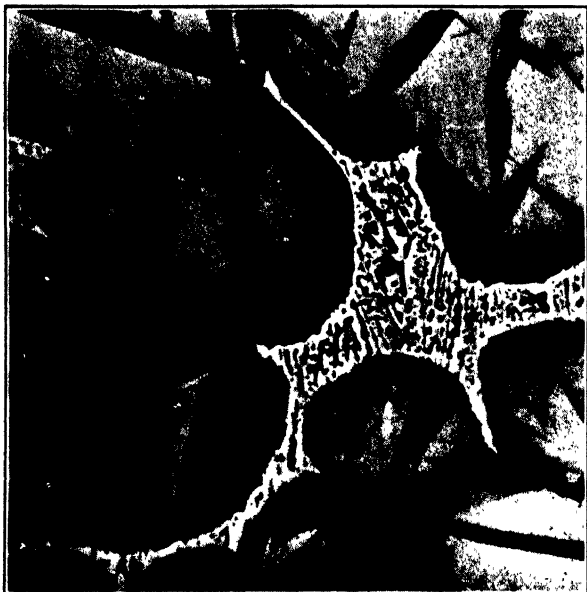


FIG. 8.—SAME FIELD AS FIG. 7. TAKEN WITH 6-MM. OBJECTIVE AND THE 10 \times OCULAR
THE MAGNIFICATION IS NOW 750 \times .



FIG. 9.—SAME FIELD AS FIGS. 7 AND 8. TAKEN WITH THE 6-MM. OBJECTIVE AND 14 \times OCULAR. THE MAGNIFICATION IS 1050 \times . IT WILL BE OBSERVED THAT IN FIGS. 8 AND 9 THE QUALITY OF THE IMAGE HAS NOT BEEN IMPAIRED BY HIGH EYEPIECING. AFTER THESE PICTURES WERE TAKEN, IT BECAME EVIDENT THAT IMPROVEMENTS HAD TO BE MADE IN THE TECHNIQUE OF POLISHING SPECIMENS FOR ULTRA-VIOLET WORK. NOTE INNUMERABLE FINE SCRATCHES RESOLVED BY THE OBJECTIVE.

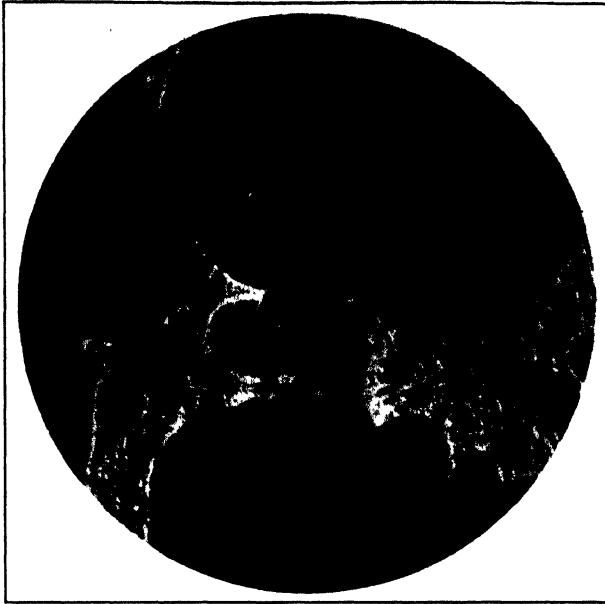


FIG. 10.—RELIEF CAN BE OBTAINED IN ULTRA-VIOLET METALLOGRAPHY BY RESTRICTING THE ILLUMINATING BEAM. TAKEN WITH THE 6-MM. OBJECTIVE AND THE 10 \times OCULAR. THE MAGNIFICATION IS 750 \times AND THE SAME SPECIMEN WAS USED AS FOR FIGS. 7, 8 AND 9.



FIG. 11.—NORMALIZED HYPER-EUTECTOID STEEL TAKEN WITH THE 6-MM. OBJECTIVE AND THE 14 \times OCULAR WITH THE MAGNESIUM SPARK. THE BLACK AREAS ARE CARBON DEPOSITED FROM THE CARBON PAPER. IN THIS CASE THE FIELD WAS NOT MOVED AFTER FOCUSING SO THE CARBON AREAS APPEAR IN THE FIELD OF VISION. THE MAGNIFICATION IS 700 \times .



FIG. 12.—SAME SPECIMEN AS FIG. 11 EXCEPT THAT THE FIELD WAS MOVED AFTER FOCUSING TO ELIMINATE THE CARBON. TAKEN WITH THE 6-MM. OBJECTIVE AND $20\times$ OCULAR WITH MAGNESIUM SPARK. THE MAGNIFICATION IS $1000\times$. NOTE THAT HIGH EYEPIECING HAS NOT AFFECTED THE QUALITY OF THE IMAGE. A SCRATCH IS RESOLVED AS A SERIES OF DOTS. THE RESULT OBTAINED COMPARES FAVORABLY WITH THE DEGREE OF RESOLUTION OBTAINED WITH THE 1.40 N.A. APOCHROMAT USING THE SAME SPECIMEN.

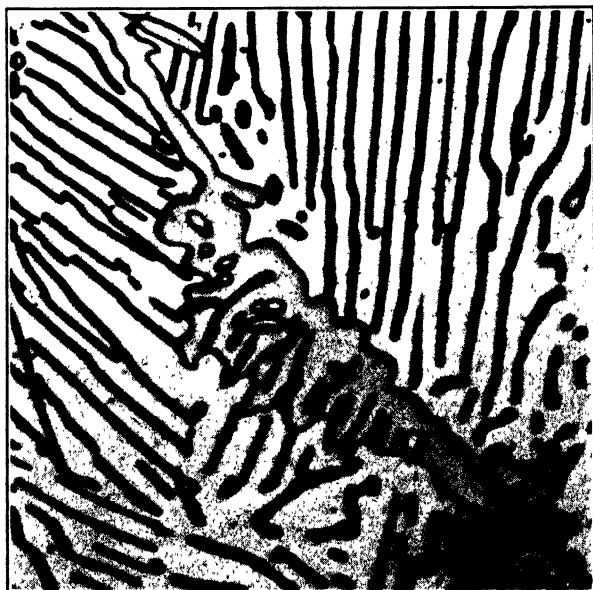


FIG. 13.—SAME SPECIMEN AS IN FIG. 12, BUT PHOTOGRAPHED WITH AN APOCHROMAT OF 1.40 N.A. USING BLUE LIGHT OF THE VISIBLE SPECTRUM. COMPARE WITH FIG. 14 TAKEN WITH THE ULTRA-VIOLET EQUIPMENT.



FIG. 14.—SAME SPECIMEN AS FIG. 12 BUT TAKEN WITH THE 2.5-MM. OBJECTIVE AND $14\times$ OCULAR USING THE CADMIUM SPARK. THE MAGNIFICATION IS $1600\times$ AND THE DEGREE OF RESOLUTION SURPASSES ANYTHING THE WRITER HAS ACHIEVED BY ANY OTHER MEANS.

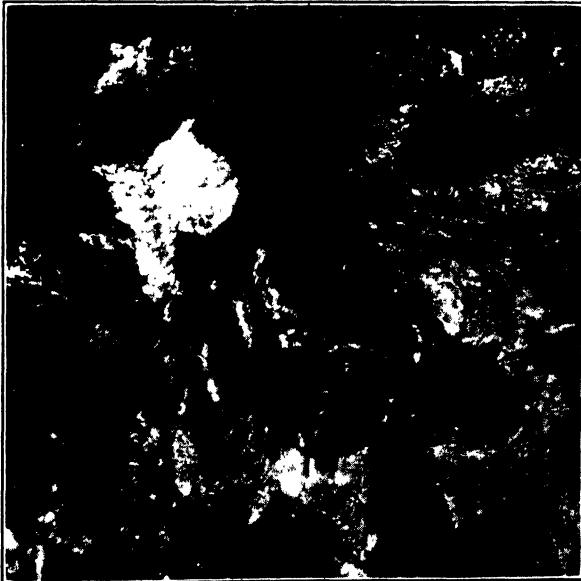


FIG. 15.—SORBITE IN EUTECTOID STEEL AT A MAGNIFICATION OF $700\times$. NOTE THAT ABSORPTION OF ULTRA-VIOLET LIGHT IS GREATEST WHERE THE STATE OF STRATIFICATION IS LEAST COMPLETE.

IDENTIFICATION OF STRUCTURES

Ultra-violet light has selective properties which should help to identify structures. It appears that certain constituents of hardened steel, for example, absorb ultra-violet light more readily than do other constituents. It is quite likely that this same characteristic will be found in connection with other metals. It is known that many colorless organic objects show the effects of selective absorption of ultra-violet light, and although they show no signs of color by white light they respond to ultra-violet light as though colored.

The writer has made many observations of iron and steel structures and can report tentatively as follows with regard to the selective characteristics of ultra-violet light. The specimens were polished and etched in the usual way.

Austenite	Reflects ultra-violet light.
Martensite, untempered	Probably absorbs ultra-violet light to some extent but much light appears to be reflected from individual needles. The needles photograph light. The mid-ribs photograph dark like troostite.
Martensite, slightly tempered	Probably absorbs ultra-violet light readily—the needles photograph dark.
Troostite	Absorbs ultra-violet light to a large extent. Troostite photographs almost black due to this selective absorption. No other constituent of hardened steel seems to absorb ultra-violet light as readily as troostite.
Sorbite	Shows less absorption than troostite but more than pearlite.
Pearlite	Reflects ultra-violet light.
Free carbides	Appear to reflect completely ultra-violet light.
Free ferrite	Appears to reflect completely ultra-violet light.

GENERAL CONCLUSIONS

The ultra-violet microscope can be said to have lived up to expectations. Crisp brilliant images can be obtained which surpass in quality those obtainable with the apochromatic system. The potential resolving ability of the monochromats can be realized in practice and the practical application of the ultra-violet microscope should develop much new information. The ultra-violet microscope is the most complicated of any within the realm of technical or scientific microscopy. It requires a highly developed technique for its successful manipulation and the specimens must be prepared with great care. The ultra-violet equipment appears to have a potential resolving ability probably greater than twice that of the apochromatic system.

DISCUSSION

H. S. GEORGE, Long Island City, N. Y. (written discussion).—The recent interesting paper by F. F. Lucas, "An Introduction to Ultra-violet Metallography," represents pioneering work for which all should be grateful.

The fact that a bas-relief is imparted to the appearance under certain conditions, as depicted in Figs. 10 and 14, suggests to the writer that the conditions in the optical train at times may be such as to eliminate the axial rays as in conical illumination. The effect of the axial rays in ordinary illumination is to mask the beneficial effect of the oblique rays, and the suggestion is here advanced that possibly this contributes in the same way, to some degree, to the exceptional results attained with ultra-violet illumination.

F. F. LUCAS.—The writer appreciates Mr. George's discussion on illumination as a helpful contribution.

The writer is inclined to believe that improvements in resolution are coming from several sources:

1. The big gain is made by virtue of the short wave-length light used. Of this there can be little question.

2. The fact that the objectives are monochromatic means that all errors of chromatic aberration are wiped out—chromatic aberrations do not appear when single wave-length light is used. The monochromats are corrected for spherical errors and the writer is inclined to believe that, as a whole, a very high order of purity in the correction of the objectives is possible. This would improve definition.

3. Fluctuations in the path of the spark between electrodes probably imparts, to some degree, obliquity to the rays and thus promotes improvement in resolution. It is quite conceivable that axial rays may be entirely absent if the spark fluctuates widely.

It also is probable that variations in the intensity of the illumination result as the spark fluctuates.

The difficulty in the present ultra-violet equipment is to obtain real critical illumination. Even very slight decentering produces flares and inequalities of illumination, which are wholly ruinous to definition such as Fig. 14 shows. At present we are working toward greater mechanical precision in the adjustment of the optical parts of the illuminating train with the object of improving conditions.

The Effect of Annealing upon the Hardness of Cold-worked Ingot Iron

BY CHARLES Y. CLAYTON, ROLLO, Mo.*

(New York Meeting, February, 1926)

A study of the literature shows that the greater part of research work on annealing of cold-worked iron has been for the purpose of studying the effect on grain-size and properties other than hardness. No reference has been found of experimental work of the same nature as that explained in this short paper.

The material used throughout was Vismara iron, an iron containing 0.03 carbon and made several years ago by the Inland Steel Co. One-half inch stock was cut into cylinders $\frac{3}{4}$ in. long. The cylinders were then compressed for 60 sec. in a Reihle testing machine under loads as indicated below:

SERIES	COMPRESSION, POUNDS	AVERAGE LENGTH, INCHES
1	10,000	0.693
2	15,000	.599
3	20,000	.501
4	25,000	.426
5	30,000	.378
6	35,000	.351
7	40,000	.311

Fig. 1 shows these cylinders after compression. Each series consisted of 17 specimens lettered O, B, C, D, E, F, G, H, I, J, K, L, M, N, P, Q and R. One specimen of each series was reserved for study of the properties in the cold-worked condition. The other specimens were annealed in a Hump furnace for $\frac{1}{2}$ hr. at the following temperatures:

LETTERS	TEMPERATURE, ° C.	LETTERS	TEMPERATURE ° C.
B.....	250	J.....	650
C.....	300	K.....	700
D.....	350	L.....	750
E.....	400	M.....	800
F.....	450	N.....	850
G.....	500	O.....	900
H.....	550	P.....	950
I.....	600	Q.....	1000

* Professor of Metallurgy and Ore Dressing, Missouri School of Mines and Metallurgy.

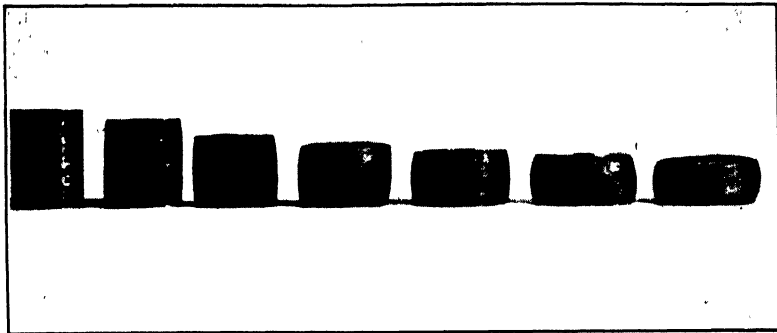


FIG. 1.—CYLINDERS OF 0.03 C STEEL AFTER COMPRESSION AT 10,000 TO 40,000 POUNDS.

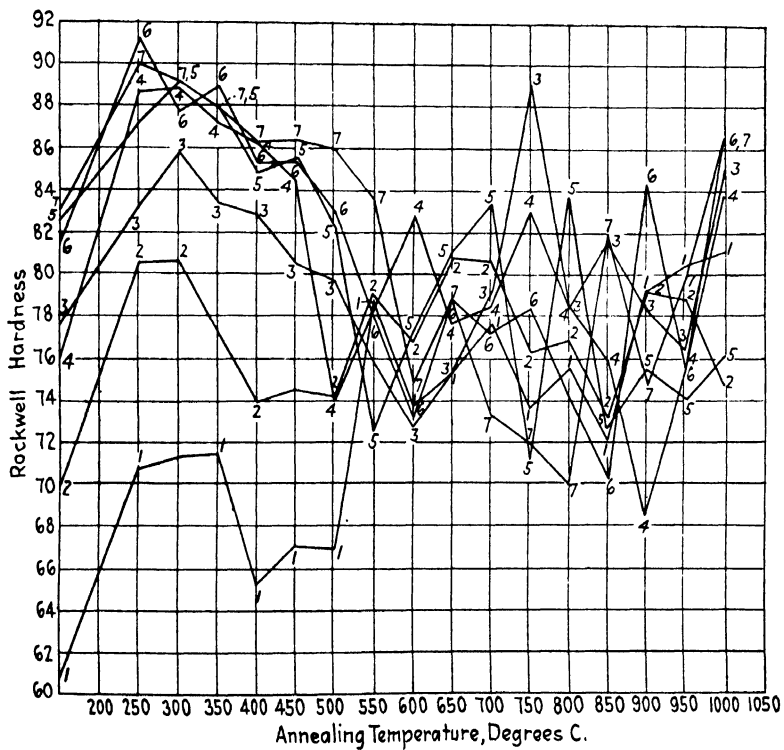


FIG. 2.—CURVES SHOWING ROCKWELL HARDNESS FOR THE SEVEN SERIES OF STEELS TESTED AT DIFFERENT ANNEALING TEMPERATURES.

After annealing the specimens were polished and etched and the grain-size¹ of each was measured. A plot of these values does not bring out anything of interest.

As it was felt that a study of the hardness of these specimens might bring forth some interesting data, tests were made both with the Brinell and the Rockwell testing machines. (Rockwell tests were made at the laboratories of Wilson-Maeulen.) In as much as a number of Rockwell tests could be made upon each specimen these values have been plotted rather than Brinell.

Rockwell values are given in Table 1 and plotted in Fig. 2.

OBSERVATIONS

Cold compressed iron (0.03 carbon), regardless of the amount of cold work, hardens upon being annealed at a temperature within the blue-heat range² between 250° C. and 425° C.

Samples compressed under loads of 20,000, 30,000, 35,000 and 40,000 lb. respectively, soften upon being annealed between 500° C. and 600° C.

Samples compressed under loads of 10,000 and 15,000 lb. did not soften upon being annealed.

TABLE 1.—*Rockwell Hardness of Ferrite after Compressing with Various Loads Followed by an Anneal*

Annealing Temperature, °C	Compression, Pounds per Sq. In.						
	10,000	15,000	20,000	25,000	30,000	35,000	40,000
None	60.7	69.8	77.7	75.9	82.6	81.5	83.1
250	70.7	80.5	83.2	88.6	87.2	91.2	89.9
300	71.3	80.6	85.8	88.8	89.1	87.7	89.1
350	71.5	77.3	83.4	87.2	87.9	88.9	87.9
400	65.2	74.0	82.8	86.1	84.8	85.3	86.3
450	67.1	74.5	80.3	84.4	85.5	85.4	86.4
500	66.9	74.2	79.7	73.9	82.1	82.9	86.0
550	78.7	79.0	75.8		72.5	77.9	83.6
600	73.7	76.8	72.7	82.7	77.2	73.0	74.9
650	75.2	80.8	75.2	77.7	81.0	78.8	78.7
700	77.6	80.6	79.1	78.4	83.3	78.2	73.3
750	73.5	76.2	89.0	82.9	71.2	78.3	71.9
800	75.5	76.4	78.4	78.4	83.7	74.0	70.0
850	72.1	73.2	81.6	75.9	72.6	70.2	81.8
900	79.2	79.1	78.4	68.5	75.4	84.3	74.8
950	80.4	78.8	76.5	75.7	74.1	75.5	79.2
1000	81.1	74.4	85.1	83.8	76.1	86.6	86.6

¹ This work was done by F. C. Schneeberger, a student at the Missouri School of Mines and Metallurgy.

² Since this article was prepared Dr. Albert Sauveur has called attention to the fact that this work confirms some work done by himself and Dr. Lee. (The Influence of Strain and Heat on the Hardness of Iron and Steel. *Iron and Steel Inst.*, Advance proof.)

Influence of Temperature, Time and Rate of Cooling on Physical Properties of Carbon Steel.—II*

BY FRANCIS B. FOLEY,† CHAS. Y. CLAYTON‡ AND W. E. REMMERS§

(New York Meeting, February, 1926)

INTRODUCTION

DURING the summer of 1919, the late Dr. Henry M. Howe, then Chairman of the Division of Engineering of the National Research Council, organized a committee to obtain a better insight into the behavior of carbon steels under the influence of various treatments by a proper control of the time and temperature factors. During part of 1919 and 1920, work in connection with this investigation was carried on at Dr. Howe's laboratory at Bedford Hills, N. Y. During 1921 there was an enforced hiatus in the work, occasioned by the illness which resulted in Dr. Howe's death in 1922. At that time one of the present authors compiled the results of the work which had been done and this was published in 1923.¹ Following the publication of this work, it seemed desirable to carry on in the same manner an investigation of steel of C 0.75 per cent., which steel had not been as fully treated as had the other steels of C 0.34 and 0.52 per cent., used in the published work. Furthermore, certain unusual results have been obtained in the treatment of C 0.52 per cent. steel by quenching and drawing, and repetition of this part of the work seemed advisable. This has been done during the past year at the School of Mines and Metallurgy of the University of Missouri at Rolla, Mo., by a cooperative undertaking of the School and the Bureau of Mines, working in conjunction with the Committee on Heat Treatment of Carbon Steels of the National Research Council. The present paper is a report of the results obtained in this work.

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¹ Howe, Foley and Winlock: Influence of Time, Temperature and the Rate of Cooling on Physical Properties of Carbon Steel. *Trans.* (1923) 69, 722.

STEEL OF CARBON 0.75 PER CENT.

The steel used in this investigation was from the same stock of $\frac{7}{8}$ -in. round bars used and described in the original paper on this subject. It had the following composition:

C.....	0.75 per cent.	P	0.031 per cent.
Mn	0.52 per cent.	S.....	0.027 per cent.
Si.....	0.11 per cent.		

Apparatus Used

The furnace used was the identical one used in the previous research, except for a new heating element and new insulation that had to be obtained. This necessitated checking the temperature distribution within the heating element. The method of determining uniformity of heat distribution was the same as that which was described in the earlier report and the results obtained were not materially different. An indicating potentiometer was used to measure all temperatures. The thermocouple used was platinum-platinum-rhodium. Base metal couples used at first were found to decalibrate too rapidly for satisfactory work and were abandoned.

For the interesting two inches of the test specimen the variation in temperature in the furnace did not exceed 7° C. at any of the temperatures at which tests were run.

Preliminary Treatment of Specimens

The $\frac{7}{8}$ -in. round bars were cut into $5\frac{1}{2}$ -in. lengths for treatment and every piece was given a preliminary normalizing treatment, which consisted in heating to 871° C. (1600° F.) and air cooling.

Method of Procedure

The arrangement of specimens in the furnace and the general procedure (including the heating rate) used in the Howe, Foley and Winlock investigation were adhered to as closely as possible in this work.

In the previous work on this steel the A_{c_3} had been determined as 741° C. (1366° F.). In the present work the temperature of heating (T max.) was 10° C. above this A_{c_3} or 751° C. (1382° F.) The time of holding at temperature was varied from 20 min. to 1 and 2 hrs.

The following methods of cooling were used. The designating letters follow those used in the work reported by Howe, Foley and Winlock:

COOLING METHOD	APPROXIMATE COOL- ING RATE, $^{\circ}$ C. PER SEC.
A Double retarded furnace cooling.....	0.01
C Plain furnace cooling.....	0.05
E Retarded air cooling.....	0.60
F Plain air cooling.....	0.90
G Accelerated air cooling.....	1.10

An additional method of cooling, that of burying the specimens in powdered lime, was also used and will be designated "L." It gave a cooling rate of 0.28°C. per second, which is between a retarded air and a plain furnace cooling.

The methods used to obtain the above rates of cooling have been described in the previous work and will be only briefly touched upon here. The double retarded furnace cooling (A) was obtained by leaving a considerable current flowing through the furnace winding while the pieces in the furnace were cooling. Plain furnace cooling (C) was done by shutting off all the current and allowing the pieces to cool undisturbed with the furnace. A muffle, which surrounded the specimens during heating, was removed along with the specimens which cooled down within it to obtain the retarded air-cooling rate (E). Plain air cooling (F) consisted in suspending the specimens in air without the hot muffle surrounding them. A fan, blowing on the specimens as they were suspended after removal from the furnace, produced the accelerated air cooling (G). The lime cooling (L) was tried because it is a form of annealing generally in use.

The rates of cooling given in the table represent the approximate average rates in the range of temperature between 751° and 585°C. This range in every method of cooling included the passage through Ar. The rate of cooling when transformation is taking place during cooling determines the physical properties obtained, other things being equal.

All the rates of cooling used were such that automatic recording was not needed. The method of recording them was the same as that used in the work by Howe, Foley and Winlock.

Everything in this experimental work, the size of the specimens, the temperature of heating (751°C.), the rate of heating, and the composition of the steel (C. 0.75 per cent.) was maintained constant with the exception of the time of holding at temperature and the rate of cooling.

PREPARATION OF SPECIMENS

Two test pieces, one for the determination of Charpy impact values and one for the determination of tensile properties, were treated in each heat. The manner of machining the test pieces from our specimens is described in the previous report of which this is a continuation. One tensile test and four impact tests were thus obtained from each heat run. The tensile specimens were broken in a small Emery hydraulic testing machine of 230,000-pounds capacity at the Bureau of Standards by Tom W. Greene, under the supervision of R. S. Johnston.

The elongation of the bars was measured by a Ewing extensometer. The proportional limit was determined from the stress-strain diagram as that stress at which the ratio of unit stress to unit deformation ceased to be constant. The yield point was taken by the drop-of beam method, which is accurate with such a sensitive machine as the one used. The

tensile strength was determined by observing the maximum load prior to rupture. The tensile strength, proportional limit, and yield point values per square inch were based on the original cross-sectional areas of the specimens. The stress at rupture was obtained by following the falling off in load as the specimen necked down. It is computed as the load per unit of area of the reduced section of the specimen as determined after rupture took place.

The Charpy impact test specimens were broken at the Watertown Arsenal under the supervision of F. C. Langenberg.

Results Obtained

Table 1 gives the results obtained which show the same general phenomena observed in the work done on C 0.34 and 0.52 per cent. steels, already reported; they are, in general, a corroboration of that work.

Although the tendency in this carbon steel is to increase in strength, hardness and ductility with increase in cooling rate, the increase, particularly with respect to notched impact value, is not so great nor so sustained as was found to be with the steel of C 0.34 per cent. In Table 1 we have borrowed figures from the corresponding treatments reported in the investigation by Howe, Foley and Winlock, of which this paper is really a continuation. The phenomenon of increase in Charpy impact value with increase in cooling rate, up to that which we have designated as "F" (plain air cooling), agrees with the results obtained with C 0.34 per cent. steel.

An outstanding point which has developed in all these investigations is that the lowest values for all of the physical properties obtained were those resulting from a very slow rate of cooling from above the critical temperature. This applies to hardness, ductility and toughness as judged from impact-resistance values.

Magnifications of 2000 diameters showed that the fastest rate of cooling (approximately 1.10° C. per second) produced a distinctly lamellar pearlite (Figs. 1 and 2). As the rate of cooling slackens the pearlite lamellæ are broken up so that with the slowest rate used much of the cementite is spheroidal (Figs. 5 and 6). The lamellæ in the rapidly cooled specimens are not resolved at a magnification of 500 diameters (Figs. 7 and 8), which magnification is fully sufficient to resolve the cementite formation in the slower cooled specimens. The photomicrographs accompanying this article (Figs. 1 to 6 at $\times 2000$ and 7 to 12 at $\times 500$) show the breaking down of pearlite lamellæ into the globular form.^{1a}

It also appears to us from our microexamination of the specimens treated that the pearlite lamellæ become coarser and tend more towards breaking up into globules as the time of holding at the annealing temperature increases to 2 hrs.

^{1a} The notations G, G2, E, E2, etc., in connection with Figures 1 to 12, refer to the column "Cooling Method" in Table 1.

TABLE 1.—Results of Physical Tests of C 0.75 Per Cent. Steel

Average Rate of Cooling, ° C. per Sec., 751° to 585° C.	Cooling Method	Proportional Limit, Pounds per Sq. In.	Yield Point, Pounds per Sq. In.	Tensile Strength, Pounds per Sq. In.	Stress at Rupture, Pounds per Sq. In.	Extension in 27 In., Per Cent.	Contraction of Area, Per Cent.	Charpy Impact Value, Foot-pounds			Brinell Hardness No.
								Minimum	Maximum	Average	
0.00667	A	40,000	40,250	89,600	127,000	19.0	35.0	1.70	1.70	1.89	180
0.00892	A1	39,000	39,500	94,600	127,000	20.0	30.0	1.16	1.61	1.61	187
0.00718	A2	41,000	41,800	86,600	144,800	21.0	30.0	1.61	1.61	2.27	174
0.05358	C	43,500	43,920	97,400	142,000	21.0	37.0	1.99	1.99	2.85	192
0.05136	C1	42,000	43,700	100,000	137,000	19.5	33.0	1.89	1.99	1.99	194
0.05437	C2	41,000	41,900	101,000	136,000	18.5	30.0	1.61	1.89	1.99	204
	Dx	40,000		99,900	144,500	21.0	35.0	1.99	1.99	2.09	203
0.52201	E	50,500	51,000	110,000	155,000	19.0	35.0	1.99	2.56	3.15	212
0.50609	E1	50,000	51,700	113,000	152,000	17.0	30.0	1.89	2.09	2.09	219
0.53205	E2	47,000	47,350	111,500	149,000	15.0	29.0	2.09	2.09	2.18	223
0.75113	F	48,000	48,400	108,700	154,000	18.0	35.0	3.15	3.65	4.04	209
0.73451	F1	56,000	56,900	116,500	158,000	17.0	32.0	1.61	2.09	2.09	223
0.85120	F2	54,500	54,800	116,400	157,000	14.0	31.0	2.09	2.09	2.18	213
	Fx	52,000	53,000	109,400	153,000	19.0	32.8	7.19	8.30	7.75	223
	Fx	42,000		105,600		17.0	26.2	2.09	2.47	2.28	218
1.0921	G	47,000	50,000	110,600	147,500	16.0	29.0	1.99	2.18	3.55	219
	Gx	49,500	56,400	115,000	158,000	19.0	31.0	1.70	1.80	1.80	228
1.0667	G1	53,500	54,300	116,600	163,500	15.0	34.1	1.61	1.61	2.09	235
	G1x	48,000	56,000	115,500	150,000	17.0	27.8	1.99	1.99	2.09	245
1.08496	G2	57,000	58,000	124,000	162,600	17.0	29.0	2.85	3.05	3.05	245
	G2x	50,000	58,500	118,000		15.5	27.0	1.52	1.70	1.61	

NOTE.—x denotes results taken from the Howe, Foley and Winlock paper. No number behind the letter is a 20-min. holding at temperature; 1 indicates a 1-hr. holding and 2 a 2-hr. holding at temperature. T max. in all tests 751° C.



FIG. 1.—STEEL CONTAINING 0.75 PER CENT. C, T MAX. 751°C ., HELD 20 MIN., ACCELERATED AIR COOLING (G). $\times 2000$.



FIG. 2.—STEEL CONTAINING 0.75 PER CENT. C, T MAX. 751°C ., HELD 20 MIN., ACCELERATED AIR COOLING (G2) $\times 2000$.

DISCUSSION

The best combination of physical properties obtained in this work resulted from plain air cooling (F) and is associated with a fine condition of lamellar pearlite. As the lamellæ break up into globules due to the slower rates of cooling, the steel becomes softer and the Charpy values are lowered.

Pearlite probably does not form in specimens cooled at faster rates than those we have used in this work. Such rates produce troostitic, sorbitic, and martensitic structures which give hardness combined with

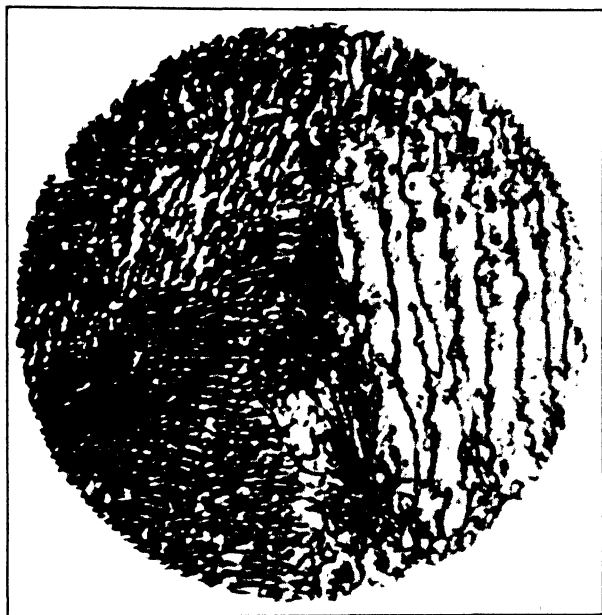


FIG. 3.—STEEL CONTAINING 0.75 PER CENT. C, T MAX. 751° C., HELD 2 HR., RETARDED AIR COOLING (E2). $\times 2000$.

low notched impact values. These structures are the result of a marked lowering of the A_r temperature. This marked lowering of the A_r causes the formation of a very great number of nuclei within the undercooled austenite, which nuclei grow slowly because of the low temperature. The limit of undercooling, which may be followed by transformation, produces martensite with crystals of colloidal dimension.

Just as it takes a certain amount of undercooling of austenite to produce the values of nuclei number and linear rate of crystallization which result in martensite, troostite and sorbite, so it would seem that a certain degree of undercooling is necessary for the formation of lamellar pearlite, and that when undercooling is minimum, lamellar pearlite will

not form but spheroidal cementite result instead. This would mean that the ultimate stable product of cooling through the critical temperature is spheroidal cementite plus ferrite and not pearlite. On the other hand, possibly, pearlite always forms and then, as in our slowest coolings, spheroidizes during the retarded cooling after passing through A_r .

The former conclusion is suggested by the fact that under a given set of slow cooling conditions, the specimen which has been held longest above the critical temperature tends to a greater degree of spheroidization. The longer holding period causes a greater degree of diffusion of carbon in the austenite and as a consequence there are fewer carbon-rich areas to

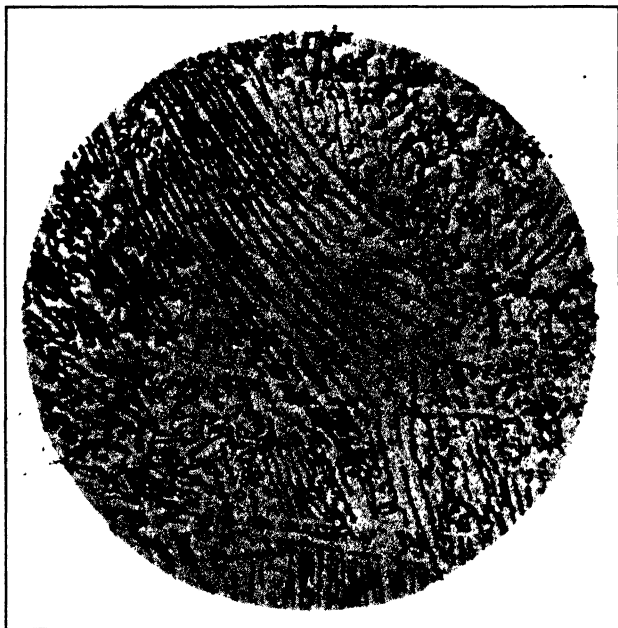


FIG. 4.—STEEL CONTAINING 0.75 PER CENT. C, T MAX. 751° C., HELD 20 MIN., RETARDED AIR COOLING (E). $\times 2000$.

retard the transformation. Under very slow cooling conditions the transformation starts at a higher temperature because of both factors, the lack of high-carbon areas, which would tend to retard transformation, and the slowness of cooling, which enables the transformation to take place when it is due. It would seem that spheroidization which took place below the A_r temperature would not be affected by the length of stay above the critical temperature and that, therefore, the degree of spheroidization under given conditions of cooling ought to be the same regardless of the time of holding above the critical temperature. Very possibly a combination of the two factors produces the spheroidal condition of cementite. The combination of high temperature, prolonged holding,

and very slow cooling would probably produce spheroidal rather than lamellar cementite.

For the best combination of physical properties to be obtained from annealing carbon steels, the steel will first be normalized thoroughly, reheated to the lowest point practical above the critical temperature, held a very short period of time (depending on size of piece being treated), and then cooled at the fastest rate which will permit lamellar pearlite to form. Probably a piece first put into the sorbitic state by a quench and draw presents the most homogeneous condition to start out with, but such steel would probably have better physical properties than could be obtained by annealing. The prevalent practice of normalizing steel prior to final treatment is no doubt beneficial even when the final treatment is to be a simple annealing.

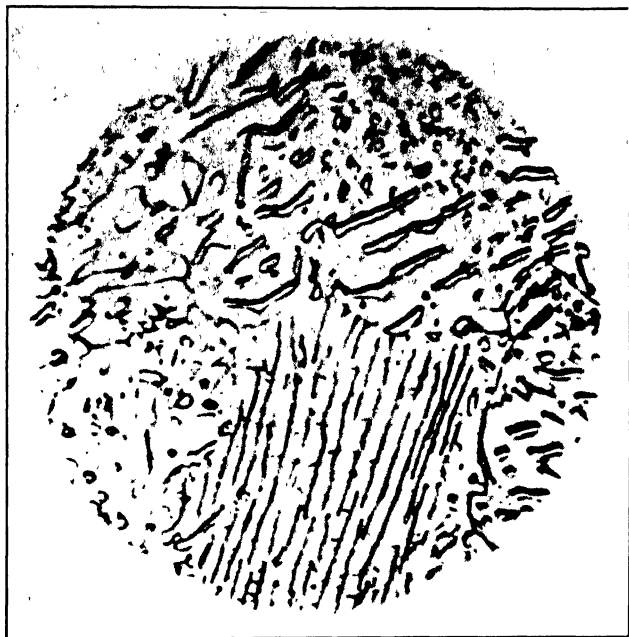


FIG. 5.-STEEL CONTAINING 0.75 PER CENT. C, T MAX. 751° C., HELD 20 MIN., RETARDED FURNACE COOLING (A). $\times 2000$.

TESTS OF STEEL OF CARBON 0.52 PER CENT.

Effect of Quenching Temperature on the Impact Values of Drawn Steel

In the work already cited of Howe, Foley and Winlock, extraordinary impact-test values were obtained with C 0.52 per cent. steel when quenching from very high temperatures was followed by drawing at 675° C. (1247° F.). In that work specimens $\frac{7}{8}$ in. round by $5\frac{1}{2}$ in. long were first given a normalizing treatment consisting in heating to 900° C. (1652° F.), and air cooling; then a number of specimens were

quenched in water from 780° C. (1436° F.), 845° C. (1553° F.), 910° C. (1670° F.), and 975° C. (1787° F.) and subsequently drawn at 300° C. (572° F.), 450° C. (842° F.), 525° C. (977° F.), and 675° C. (1247° F.).

Specimens drawn at 300° C. showed a lowering of impact value as the temperature at which they had been quenched increased. The higher drawing temperatures gave specimens whose impact value increased as the temperature from which they had been quenched increased. For example, a specimen drawn at 675° C. following a quench in water from 780° C. gave an average impact value of but 5.09 ft.-lb., whereas the same drawing following a quench in water from 975° C. gave an impact value of 23.80 ft.-lb. These results seemed to us extraordinary and

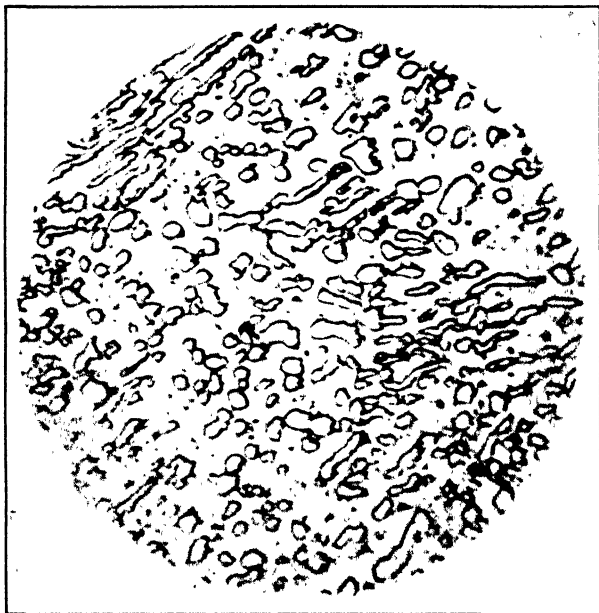


FIG. 6.—STEEL CONTAINING 0.75 PER CENT. CARBON, T MAX. 751° C., HELD 2 HR., RETARDED FURNACE COOLING (A2). $\times 2000$.

we have, therefore, repeated the work in part and carried the quenching temperature higher.

The quenching temperatures used in our present experiments were 845° C. (1553° F.), 975° C. (1787° F.), and 1040° C. (1904° F.). The time of holding at the quenching temperature was 10 min. and the specimens were normalized as in the previous work by air cooling from 900° C. The heating was carried out in the same furnace and in the same manner as described in the original work. Prior to quenching, the water was started circulating vigorously and remained in circulation during the cooling of the specimens. Two drawing temperatures were used;

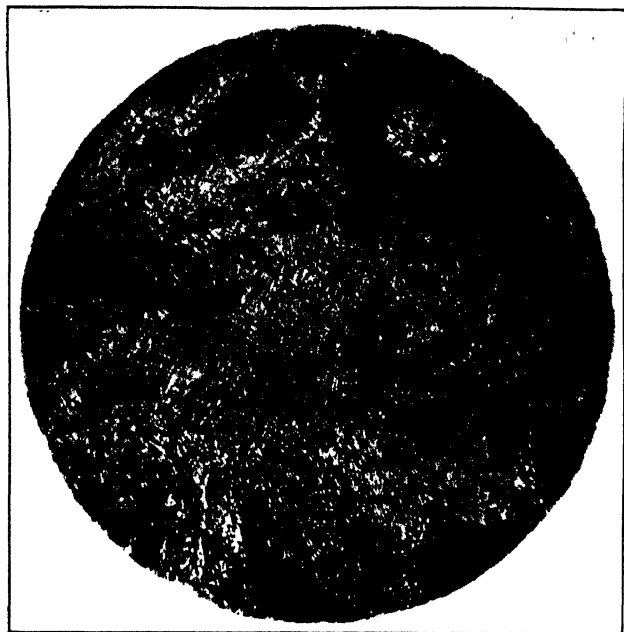


FIG. 7.—STEEL CONTAINING 0.75 PER CENT. C, T MAX. 751° C., HELD 20 MIN., ACCELERATED AIR COOLING (G). $\times 500$.

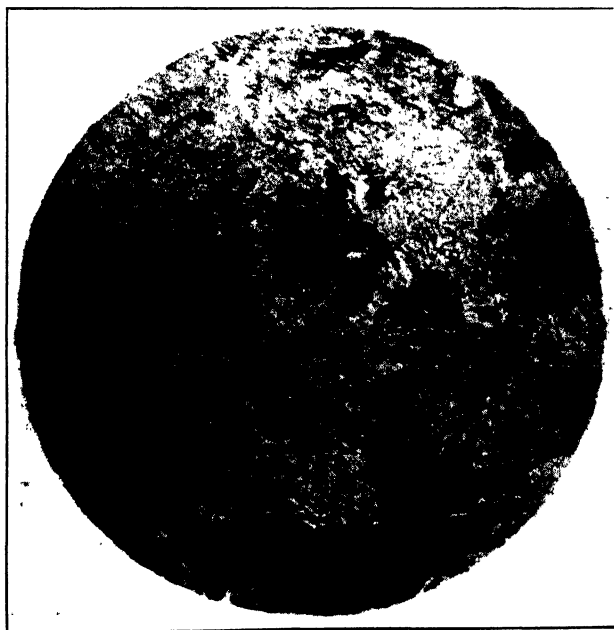


FIG. 8.—STEEL CONTAINING 0.75 PER CENT. C, T MAX. 751° C., HELD 2 HR., ACCELERATED AIR COOLING (G2). $\times 500$.

450° C. (842° F.), the holding time being 30 min., and 675° C., the holding time being 10 min. as before. To repeat all the drawings used in the previous work was not considered necessary. Only such are used as seemed necessary to check the general phenomenon evidenced by the results which have been published. Our results are given in Table 2.

All of our impact values are higher than those obtained by similar treatments in the work of Howe, Foley and Winlock. The reason for this probably lies in the fact that their specimens were quenched in still water, whereas our specimens were quenched in well agitated water. For the lower drawing temperature, and for the low quenching temperature, the spread of impact value is wider than obtained in the work of the previous investigators.

TABLE 2.—*Impact Values of Quenched and Drawn Steels Containing 0.52 Per Cent. Carbon (Composition 0.52 Per Cent. C, 0.55 Per Cent. Mn, 0.22 Per Cent. Si, 0.030 Per Cent. P, and 0.029 Per Cent. S)*

Quenched in Water from ° C.	Speci- men No.	Impact Value (Charpy), Foot-pounds					
		Minimum		Maximum		Average	Grand Average
Quenched as shown and drawn at 450° C. (842° F.), 30 minutes; air cooled							
845	1	3.95	5 16	9 66	12 38	7 79	8 25
	2	4.14	7 96	9 90	12 86	8 72	
975	1	10.36	11 19	11 78	11 90	11 31	11 18
	2	10.60	10 72	10.83	12 02	11.04	
1040	1	10.36	10.48	10.83	11.19	10.72	10.75
	2	9.55	11.19	11.19	11.19	10.78	
Quenched as shown and drawn at 675° C. (1247° F.), 10 minutes; air cooled							
845	1	10.02	12.98	16.11	18.07	14.30	13.39
	2	9.55	10.13	13.22	15.47	12.09	
975	1	24.74	25.32	26.06	27 55	25.92	26.04
	2	25.03	26.35	26.50	26.80	26.17	
1040	1	24.88	25.03	26.80	27.25	25.99	25.44
	2	24.45	24.45	24.74	25.91	24.89	

The wider spread of values for the specimens quenched from 845° C. may be accounted for by the fact that steel of this carbon content requires a severe quenching in order to produce full hardness, or, what is the same thing, approximately complete martensitization. Still water did not supply the proper conditions in the previous work and circulating water provided an approach to the desired condition for use only on the end of the specimens which entered the water first. The effect of this is more

pronounced in the specimens which were drawn at the lower temperature, because the influence of the conditions under which the specimens were hardened is still quite marked. It is less marked when the drawing temperature is raised to 675° C.

More severe quenching is required to produce full hardness by quenching carbon steels from a low temperature than when the quenching temperature is increased. Therefore, we suppose that while the conditions which prevailed in our work fell somewhat short of those necessary for the production of full hardness by quenching from 845° C., these same conditions were more nearly ideal for the quenches from 975° and 1040° C. Therefore, we have more uniform results from the specimens quenched from the higher temperatures.

The values we have obtained are a general corroboration of the results reported by Howe, Foley and Winlock.

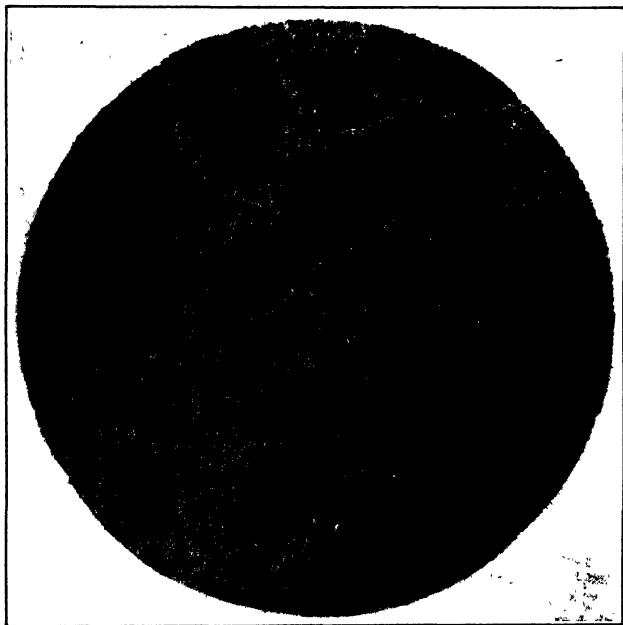


FIG. 9.—STEEL CONTAINING 0.75 PER CENT. C, T MAX. 751° C., HELD 20 MIN., RETARDED AIR COOLING (E). $\times 500$.

DISCUSSION

The present work shows, as did the previous work in which one of the present authors was engaged, that higher values for impact resistance are obtained with this steel of C 0.52 per cent. if a drawing at 450° C. to 675° C. is preceded by quenches in water from temperatures in the neighborhood of 1000° C. than when the preparatory hardening is done from temperatures nearer but above the A_{c3} . This procedure is con-

trary to the usual admonition that quenching for hardening should always be done from temperatures as near but above the Ac_3 as possible. Whether this phenomenon is a peculiarity of the particular steel we have used or not we are unable to say, but we have no reason to think that it is. The steel is carefully prepared acid open-hearth steel of normal composition and is representative of good commercial material as far as we are able to tell through careful observations made throughout its production and subsequent preparation. Only a repetition of the work, using other melts of steel of like carbon content, can settle this point.



FIG. 10.—STEEL CONTAINING 0.75 PER CENT. C, T MAX. 751° C., HELD 2 HR., RETARDED AIR COOLING (E2). $\times 500$.

This steel did show, under the microscope, that some of the proeutectoid ferrite was banded in a segregated form as shown in Fig. 13. We hesitate very much to attribute this behavior under impact stress to banded ferrite, although it might well be caused by it. It is a fact that commercial carbon steel bar-stock of hypoeutectoid composition generally contains banded ferrite and, therefore, these findings may have a broad application.

We suspect that when steel of this kind is to be used in the "as quenched" condition or after drawing at a temperature as low as 300° C., hardening would best be done at the lowest temperature which will produce the desired hardness. When the drawing is to be done at higher

temperatures probably quenching would best be done, if practical, at considerably higher temperatures, as this work shows. The difficulty, of course, would come in the danger of cracking the steel. None cracked in the treatment of these $\frac{7}{8}$ -in. round by $5\frac{1}{2}$ -in. long specimens, but pieces of different shape probably would crack.

There are no transformations known in the solid state above the A_{c3} in steels of the composition used here. Certain changes, however, are going on with increase in the temperature of the metal. One of these changes is in the size of the individual crystals of the austenite; this change increases with temperature. The other change which occurs

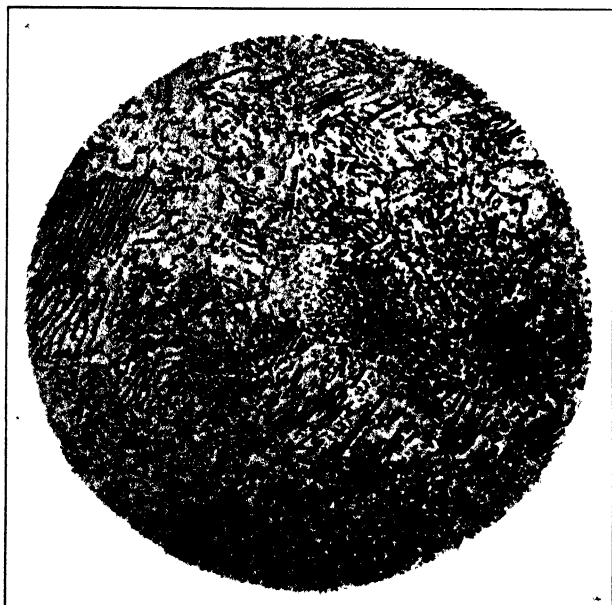


FIG. 11.—STEEL CONTAINING 0.75 PER CENT. C, T MAX. 751°C ., HELD 20 MIN., RETARDED FURNACE COOLING (A). $\times 500$.

is in the degree of homogeneity of distribution of the elements, particularly carbon, in the austenite; as the temperature rises a greater degree of homogeneity is attained. We feel quite safe in believing that an increase in the size of the individual crystals of austenite would not lead to an improvement in physical properties such as we find. On the other hand, we can well believe that the production of a more homogeneous austenite, prior to quenching by heating to a sufficiently high temperature, could easily account for the improvement.

According to French and Klopsch² a cooling rate of 220°C . per second is required to produce complete martensitization in a carbon steel of

² French and Klopsch: Quenching Diagrams for Carbon Steels in Relation to Some Quenching Media for Heat Treatment. *Trans. Am. Soc. Steel Treating*, Sept., 1924.

C 0.45 per cent. cooled from 875° C., the specimens used in their work having been $\frac{1}{2}$ -in. rounds. Water at room temperature, such as was used in our work, gives a cooling rate on $\frac{1}{2}$ -in. rounds, according to French and Klopsch, of between 110° and 150° C. per second. This rate of cooling was not rapid enough to produce complete martensitization in their C 0.75 per cent. steel. In our specimens troostite was present, even in the specimens quenched from the highest temperature we used (1040° C.). Fig. 14 shows typical acicular martensite associated with troostite in this C 0.52 per cent. steel. In the reason for the presence of troostite in these rapidly quenched steels, will probably be found the reason for the higher impact values we have obtained. French and

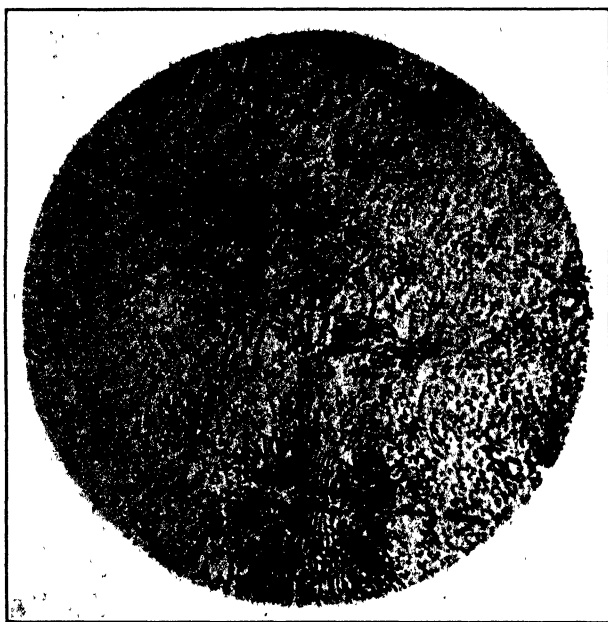


FIG. 12.—STEEL CONTAINING 0.75 PER CENT. C, T MAX. 751° C., HELD 2 HR., RETARDED FURNACE COOLING (A2). $\times 500$.

Klopsch used the thermocouple at the center of the mass being quenched, so that the rates they obtained were the slowest that existed in the mass during cooling. The presence of microscopic quantities of troostite can hardly be caused by a slower rate of cooling in these localities of microscopic size. They are most likely the result of an heterogeneous austenite. Certain spots have a low carbon content, and, therefore, a higher rate of cooling than that which exists in the mass is necessary in order to produce martensite in such localities. We cannot harden pure iron because we are unable to lower the transformation during cooling to the extent that we can when carbon is present, and we produce troostite amidst martensite in these medium-carbon steels because not enough

carbon is in the troostitic areas to aid in lowering the transformation to the temperature at which martensite is produced.

Portevin and Garvin³ showed that a slower rate of cooling can be used in producing complete martensitization if the temperature of quenching is increased. This would indicate that at higher temperatures a degree of homogeneity is attained that is not present at lower temperatures, and it is to the more uniform distribution of carbon, which we have thus obtained, that we attribute these higher impact values. In the high drawing temperatures which follow the quenching, we are not concerned with the crystal size of the austenite which preceded the quench-

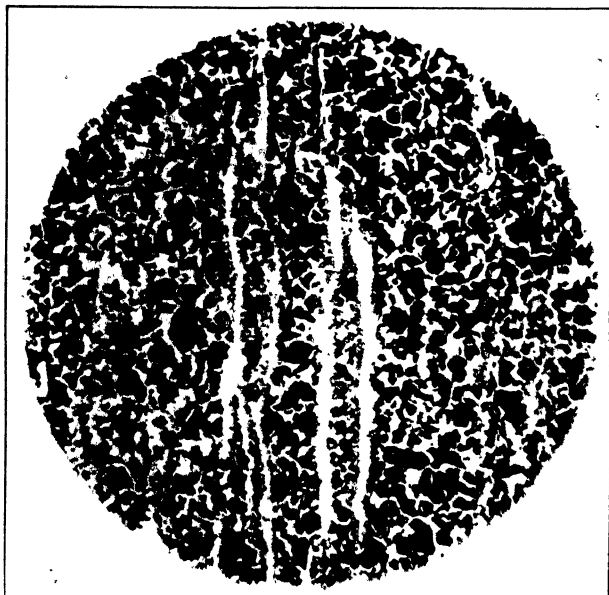


FIG. 13.-LONGITUDINAL SECTION OF ROLLED BAR OF STEEL CONTAINING 0.52 PER CENT. C. $\times 150$.

ing. The influence of that is entirely lost. No doubt its influence is found in the martensite which succeeded it and perhaps to some extent, in the next generation, troostite, but practically none remains in the high temperature sorbite. The segregation of carbon, however, exists in a modified form throughout all of the subsequent modifications. In the sorbite it is a segregation of carbide of iron, and a segregation of carbide means localized impoverishment of carbide, for the gain in carbide by one locality is at the expense of another.

If, in order to produce the best impact values in quenched and drawn steels, it is necessary to go to such high temperatures and quench there-

³ Investigations on Influence of the Rate of Cooling on Hardening of Carbon Steels. *Jnl. Iron Steel Inst.* (1919), **99**, 551.

from, considerable advantage will be lost in the case of intricately shaped pieces because of the great danger of cracking. If our reasons for the increase in toughness found is correct, there should be no loss incurred



FIG. 14.—TROOSTITE IN MARTENSITE OF STEEL CONTAINING 0.52 PER CENT. C, QUENCHED IN WATER FROM 1040° C. $\times 2000$.

by allowing a piece to cool uniformly to a lower temperature (yet above the A_r) and then quenching. Once the desired degree of homogeneity

is established at the high temperature, one would not expect the diffused carbon to segregate again at a lower temperature while still above Ar, unless too close an approach to Ar were made.

In this latter event, perfect homogeneity of austenite not being attained perhaps in any event, the allotropic transformation would commence in such spots of lower carbon as might chance to exist. However, there is room for experimentation here and we propose to try it. Of course, as we have stated before, this is only practical where a high drawing temperature is used to produce a tough steel. It is no aid either in steels which are used in the "as hardened" state, or in those which are drawn at low temperatures. Neither is it of use in annealing steels of this type for, in very slow coolings, ferrite forms at the borders of the transformed austenite crystals and, if these are large, a coarse ferrite segregation results. In other words, the diffusion attained at the high temperature is nullified by the segregation of ferrite at the crystal boundaries during cooling, and the coarseness of the austenite crystallization is accentuated by its presence there. This condition is a special case but is one which, it seems to us, has broad application in industry.

Effect of Air Gap in Explosion System on Production of Neumann Bands*

FRANCIS B. FOLEY† AND J. E. CRAWSHAW,‡ SIGNAL MOUNTAIN, TENN.

(New York Meeting, February, 1926)

IN THE first report¹ disks of steel of known composition and history were exposed, under carefully prescribed conditions, to impacts of explosion products resulting from the explosion of 50-gm. charges of explosives having well-determined rates of detonation, or to impacts of a weight of known mass, falling through measured distances. There were available at the Bureau of Mines Experiment Station five explosives, having rates of detonation of 5716, 4470, 3190, 2296, and 1523 meters per second. It being desired to continue this exposure downward, and no explosives with a lesser rate of detonation being at hand, resort was had to the impact of a falling weight, the differences in the velocity of impact being attained by varying the height from which the weight was allowed to fall. It was expected by this means to demonstrate experimentally that the development of Neumann bands was determined by the suddenness of the deformation of the metal in which they were produced. But while progressive deformations were obtained with the explosive charges, the falling-weight method failed because the tup was progressively deformed, also the disks were so flattened as to be unfit for metallographic examination.

A return, therefore, has been made to the use of explosives as the source of energy, an air-gap being interposed between the charge of explosive and the disk, as the effect diminishes as the function of the distance between the charge and the object on which the products of its explosion, or the shock wave from its detonation, impinge. The details of the arrangement of the tests by the air-gap method were the same as those described by Foley and Howell,² except that after the system had been set up and the desired apparent specific gravity for the explosive attained by tamping it, the small lead block, with the steel disk adhering

* Published by permission of the Director of the Bureau of Mines.

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¹ F. B. Foley and S. P. Howell: Neumann Bands as Evidence of Action of Explosives on Metal. *Trans.* (1923) **68**, 891.

² *Op. cit.*, 899.

to it (because of the vaseline coating regularly used in the Bureau of Mines small lead block test), was slipped down; or, the explosive charge, with its contained detonator, which adhered firmly to the walls of the paper tube, was, with the tube, slipped up until the desired measured gap was secured.

This report deals with eight specimens, or disks, numbered 1 to 8 air gap, of the same shape and material as was used in the previous work. The explosive used was 60-per cent. straight nitro-glycerine dynamite, in 50-gm. charges, tamped to an apparent specific gravity of 1.21, and fired by No. 7 electric detonators. Specimen 1 represents the original material, not subjected to the impact of explosion. The explosive was detonated while in contact with the surface of specimen 2, and at the distances above the surface of specimens 3 to 8 here shown.

SPECIMEN NUMBER	AIR SPACE, MILLIMETERS	DEPRESSION OF LEAD BLOCK, MILLIMETERS
1 air gap.		
2 air gap	0	20.75
3 air gap	4	17 00
4 air gap	8	12 00
5 air gap	16	11.25
6 air gap	32	6 00
7 air gap	64	3.25
8 air gap	128	2 00

The last column records the extent of the depression of the lead block on which the specimen was supported.

Following the practice in the first investigation, all the specimens were photographed, at 200 diameters, at three points along the axis of the disks, designated as positions 1, 2 and 3. Position 1 is 1 mm. from the front face, or that face of the specimen that was toward the explosive; position 2 is at the center of the specimen; and position 3 is 1 mm. from the back face, or that face of the specimen that was down, or away from, the explosive.

Specimen 2, which had no air space between it and the explosive, shows numerous Neumann bands. With an air space of 4 mm. the number of bands was considerably less, as shown in specimen 3. With an increase in the air space up to and including 16 mm., there is little change in the appearance under the microscope as shown by the photomicrographs of specimens 3, 4 and 5. There are fewer bands, particularly in position 2, with an air gap of 32 mm., and the number seems to decrease gradually until with an air gap of 128 mm. (specimen 8), no bands appear at the center of the specimen, and but a few exist in positions 1 and 3. The lowest impact velocity used in this work is then sufficient to produce some Neumann bands.

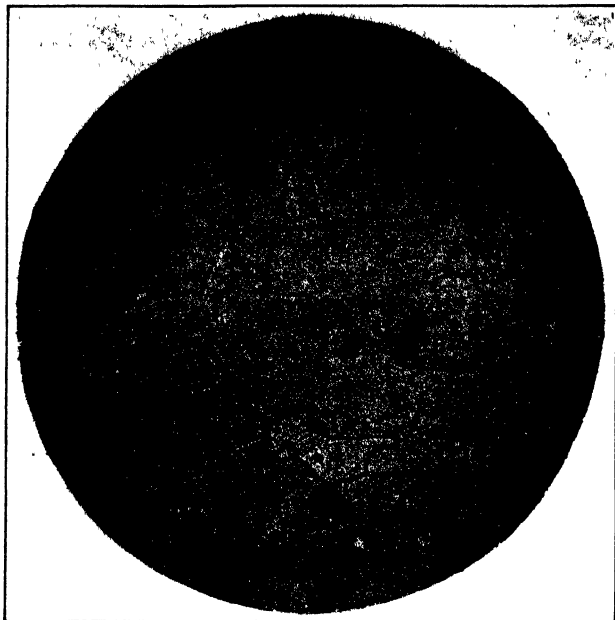


FIG. 1.—SPECIMEN 1, WHICH WAS NOT SUBJECTED TO EXPLOSIVE IMPACT. $\times 200$



FIG. 2.—POSITION OF SPECIMEN 2; NO AIR SPACE BETWEEN SPECIMEN AND EXPLOSIVE.
 $\times 200$.



FIG. 3.—POSITION 2 OF SPECIMEN 2; NO AIR SPACE BETWEEN SPECIMEN AND EXPLOSIVE.
× 200.



FIG. 4.—POSITION 3 OF SPECIMEN 2; NO AIR SPACE BETWEEN SPECIMEN AND EXPLOSIVE.
× 200.



FIG. 5.—POSITION 1 OF SPECIMEN 3; 4-MM. AIR SPACE BETWEEN SPECIMEN AND EXPLOSIVE. $\times 200$.

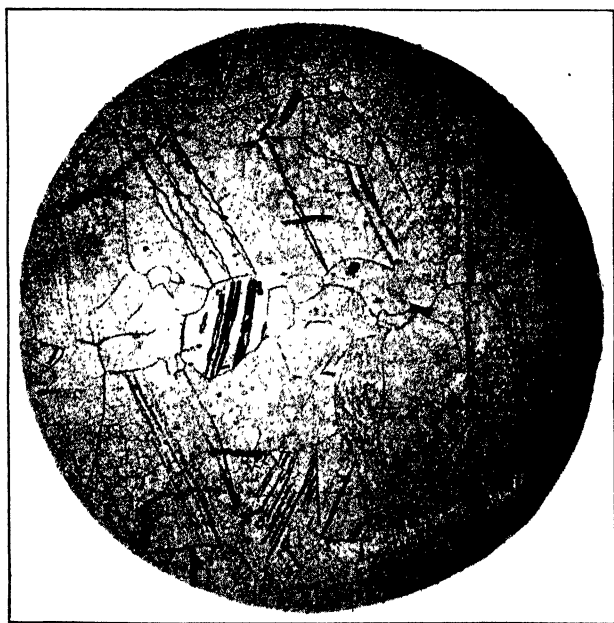


FIG. 6.—POSITION 2 OF SPECIMEN 3; 4-MM. AIR SPACE BETWEEN SPECIMEN AND EXPLOSIVE. $\times 200$.

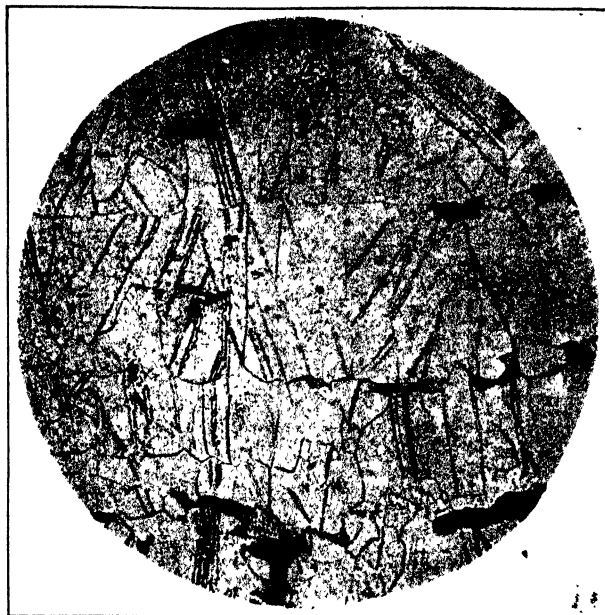


FIG. 7.—POSITION 3 OF SPECIMEN 3; 4-MM. AIR SPACE BETWEEN SPECIMEN AND EXPLOSIVE. $\times 200$.

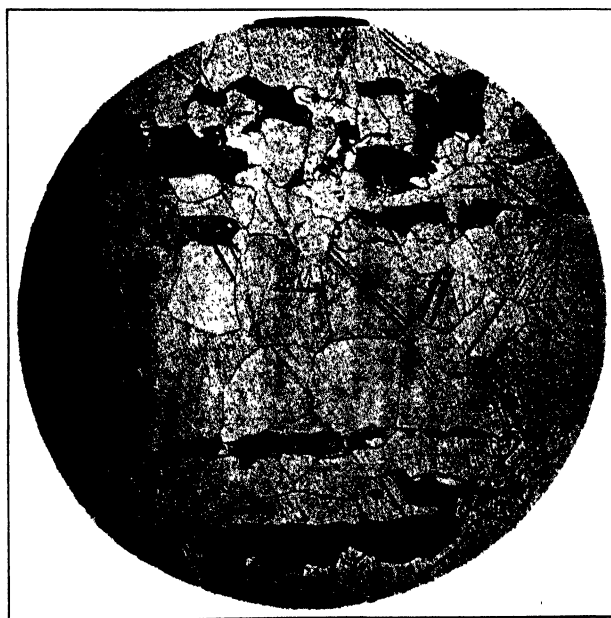


FIG. 8.—POSITION 1 OF SPECIMEN 4; 8-MM. AIR SPACE BETWEEN SPECIMEN AND EXPLOSIVE. $\times 200$.



FIG. 9.—POSITION 2 OF SPECIMEN 4; 8-MM. AIR SPACE BETWEEN SPECIMEN AND EXPLOSIVE. $\times 200$.

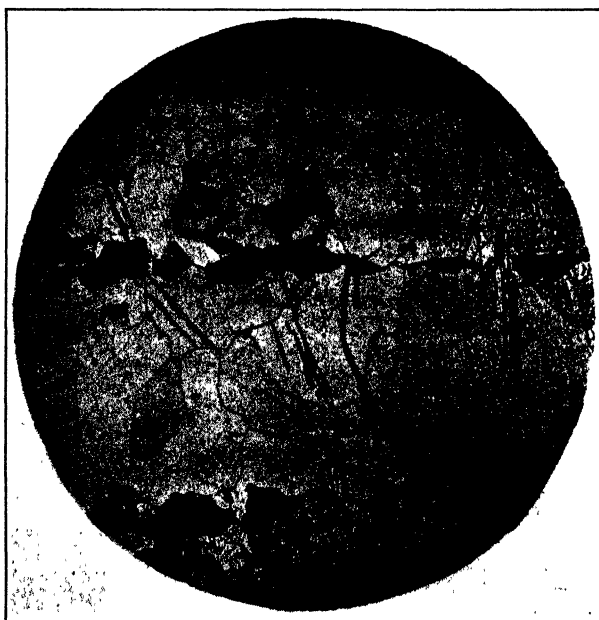


FIG. 10.—POSITION 3 OF SPECIMEN 4; 8-MM. AIR SPACE BETWEEN SPECIMEN AND EXPLOSIVE. $\times 200$.

EFFECT OF NEUMANN BANDS ON SOLUBILITY OF IRON IN
HYDROCHLORIC ACID

So far it has not been found possible to detect Neumann bands in steel that has been subjected to very sudden deformation, unless the steel contains an excess of free ferrite. Thus the examination of steel for Neumann bands by means of the microscope is confined to steel of very low carbon content in the annealed state, and it does not permit us to determine quantitatively the extent of twinning. It is known that Neumann bands are a characteristic of ferrite and that such constituents of steel as troostite, sorbite and pearlite contain ferrite. The question, therefore, arises: Are Neumann bands produced in sudden impact in these other constituents of steel, as well as in the pro-eutectoid ferrite and are we unable to detect them only because the ferrite crystals are so small that they are not visible as such under the microscope? May it not be possible to correlate the Neumann bands that we are able to see in the ferrite of low-carbon steels with some measurable property and then to use that property as a gage to measure the imperceptible Neumann bands that may be present in high-carbon and alloy steels? To say that twinning does not exist in pearlite, for example, is to say that twinning cannot be produced in ferrite when the crystal size reaches a certain minimum. If shock does not produce Neumann bands in very fine ferrite, such as that in pearlite, does it have any other effect?

In the first report of the Committee³ attention was called to the fact that Osmond and Wuth, Heyn and Bower, and Goerens have noted that the rapidity of solution of iron increases steadily with the degree of mechanical treatment to which the iron has been subjected, and that these observations suggest a possible means by which the development of Neumann bands in a specimen might be quantitatively followed. In other words, if the solubility of iron in a given solvent increases with the mechanical work previously done upon it, the degree of twinning in the different test pieces cut from the same piece of steel shafting, but each subject to a different degree of exposure to deformation, might be ascertained by the measurement of the relative rates of solution of the differently exposed specimens in the given solvent.

Specimens 1, 3, 5 and 7 air gap, of those described in the first part of this paper, were used to make a preliminary test of this solubility theory. The procedure planned was as follows: A small portion, of approximately square cross-section, was to be machined from a radial position in each of specimens 1, 3, 5 and 7 air gap. The cross-sectional area of each piece thus obtained was to be measured as precisely as possible with a micrometer. Each piece was then to be covered with an acid-resisting coating, except upon the measured surface. The piece was then to be weighed

and the measured cross-sectional area exposed to the solvent. After the determined length of exposure, the specimen was to be removed, washed, dried, and weighed and the solution titrated for iron. The loss from solution was then to be calculated as loss per square millimeter of exposed surface.

A protective coating of paraffin was used in the first experiments and the pieces were immersed in a solution of equal parts of nitric acid and water but this was unsuccessful because the acid ate in between the paraffin and the sides of the piece until portions of the paraffin were lifted off bodily so that the area attacked was unknown. The pieces were, therefore, electroplated with copper. The method used was that recommended by Rawdon⁴ for preparing thin sections for micro-examination. First, a thin layer of copper was applied in a neutral solution of cuprous cyanide and then a fairly heavy deposit in a solution of copper sulfate and sulfuric acid. The cross-sectional area of the pieces having been determined, they were copper-plated all over; then the copper was removed from the end that was to be exposed to the acid. The piece was weighed and then suspended for $\frac{1}{2}$ hr. in a solution of equal parts of hydrochloric acid and water, this solvent being used because, while it attacks iron, it does not attack pure copper. After removal and drying, the piece was again weighed and the solution titrated for iron with KMnO_4 . Each piece was suspended in a separate beaker containing in every case 25 cc. of the acid solution. The ends were again ground off and the experiment repeated, changing the time of immersion in the acid to 1 hr.; after another regrinding the specimens were immersed for 2 hr. The results were as follows:

Specimen No.	Loss in $\frac{1}{2}$ Hr		Loss in 1 Hr		Loss in 2 Hr	
	Weight	Titration	Weight	Titration	Weight	Titration
3 air gap....	0.0000806	0 0000773	0 000225	0 000262	0 000407	0.000350
5 air gap....	0.0000745	Not determined	0.000314	0.000388	0.001173	0 000249
7 air gap....	0.0000542	0.0000913	0 000119	0.000181	0 000127	0.000103
1 air gap....	0.0000419	0 000106	0.000092	0 000177	0.000123	0 000177

These results have been plotted, the result being shown in Fig. 23. No attempt is made to draw any conclusions from this preliminary work regarding the solubility of these pieces in 50:50 hydrochloric acid and water, other than to say that the results indicate that an accurate determination of the losses in dilute acid will probably show a relationship to exist between the solubility of the metal and the degree of deformation, or twinning that the specimens have undergone under the action of the explosive.

⁴H. S. Rawdon: Preparation of Small Pieces for Microscopic Examination *Chem. & Met. Eng.* (1921) **24**, 475.

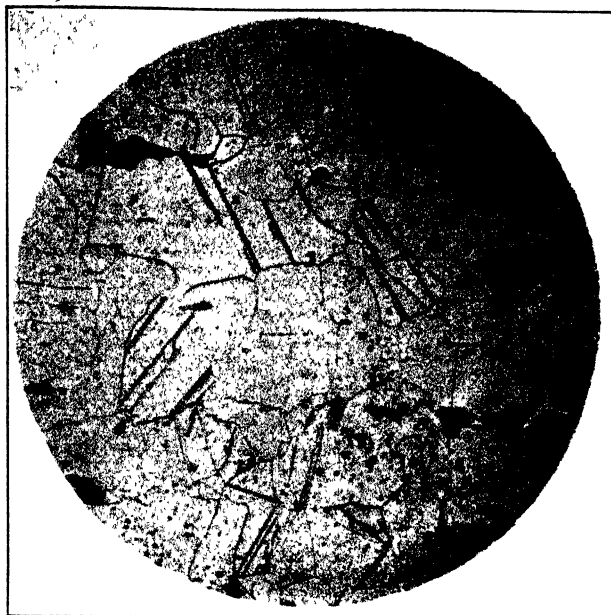


FIG. 11.—POSITION 1 OF SPECIMEN 5; 16-MM. AIR SPACE BETWEEN SPECIMEN AND EXPLOSIVE. $\times 200$.

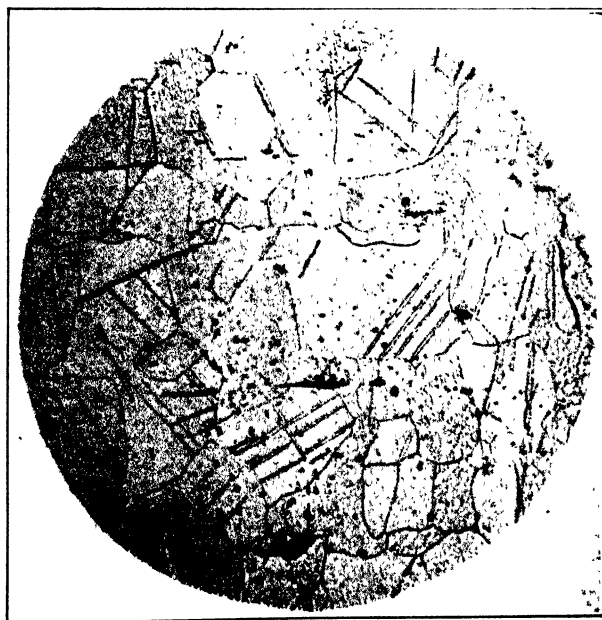


FIG. 12.—POSITION 2 OF SPECIMEN 5; 16-MM. AIR SPACE BETWEEN SPECIMEN AND EXPLOSIVE. $\times 200$.

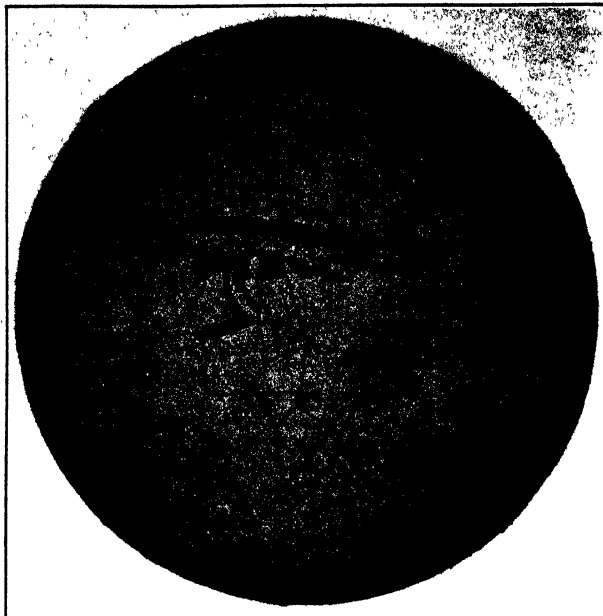


FIG. 13.—POSITION 3 OF SPECIMEN 5; 16-MM. AIR SPACE BETWEEN SPECIMEN AND EXPLOSIVE. $\times 200$.

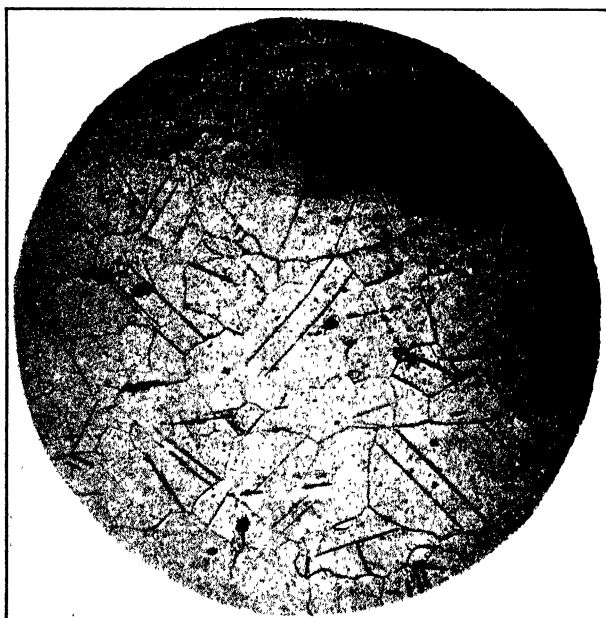


FIG. 14.—POSITION 1 OF SPECIMEN 6; 32-MM. AIR SPACE BETWEEN SPECIMEN AND EXPLOSIVE. $\times 200$.

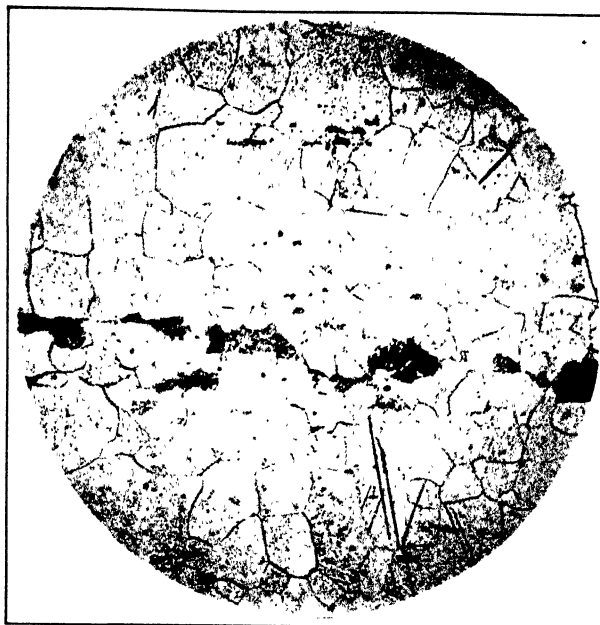


FIG. 15.—POSITION 2 OF SPECIMEN 6; 32-MM. AIR SPACE BETWEEN SPECIMEN AND EXPLOSIVE. $\times 200$.

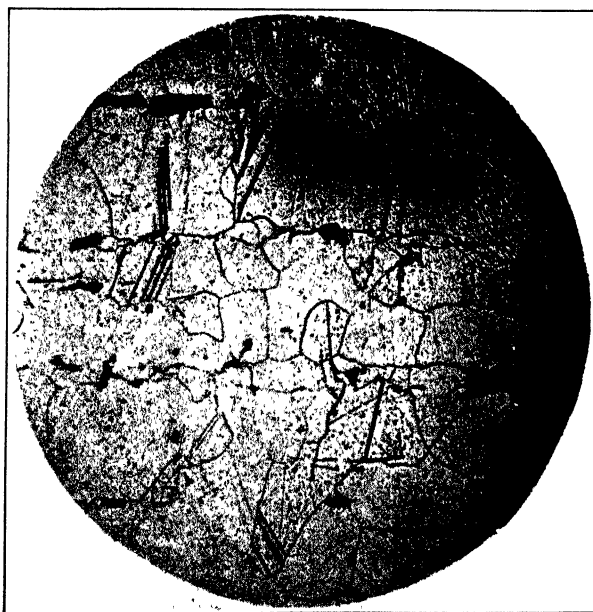


FIG. 16.—POSITION 3 OF SPECIMEN 6; 32-MM. AIR SPACE BETWEEN SPECIMEN AND EXPLOSIVE. $\times 200$.

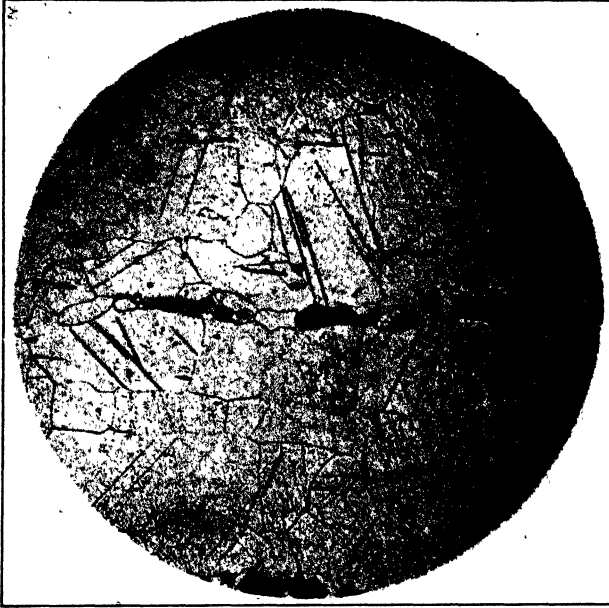


FIG. 17.—POSITION 1 OF SPECIMEN 7; 64-MM. AIR SPACE BETWEEN SPECIMEN AND EXPLOSIVE. $\times 200$.

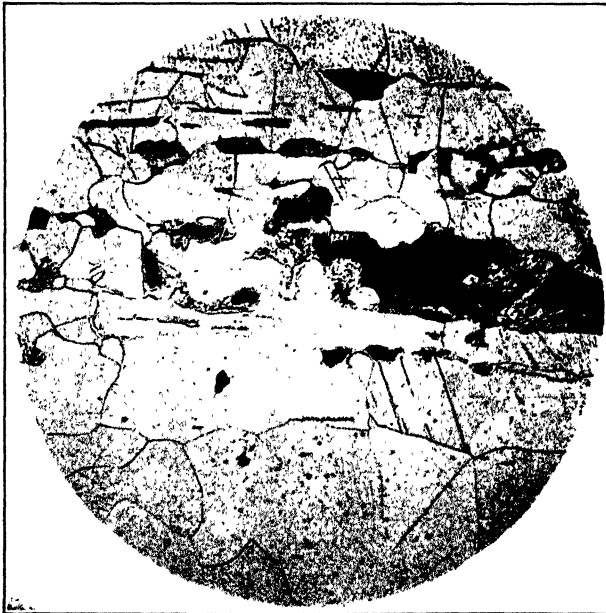


FIG. 18.—POSITION 2 OF SPECIMEN 7; 64-MM. AIR SPACE BETWEEN SPECIMEN AND EXPLOSIVE. $\times 200$.

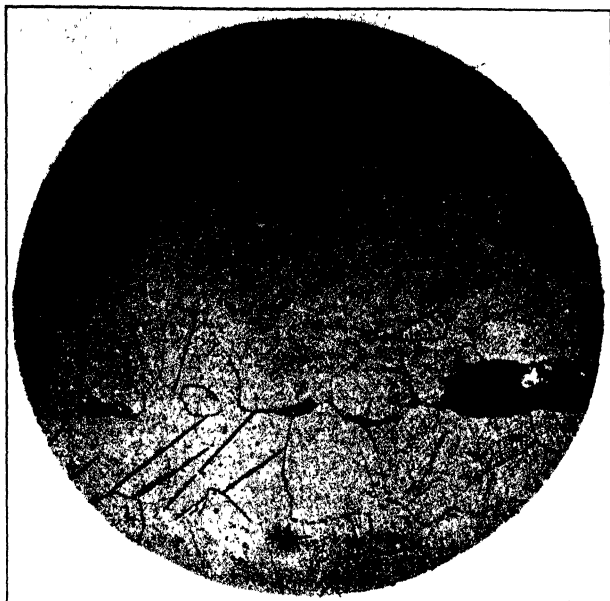


FIG. 19.—POSITION 3 OF SPECIMEN 7; 64-MM. AIR SPACE BETWEEN SPECIMEN AND EXPLOSIVE. $\times 200$.

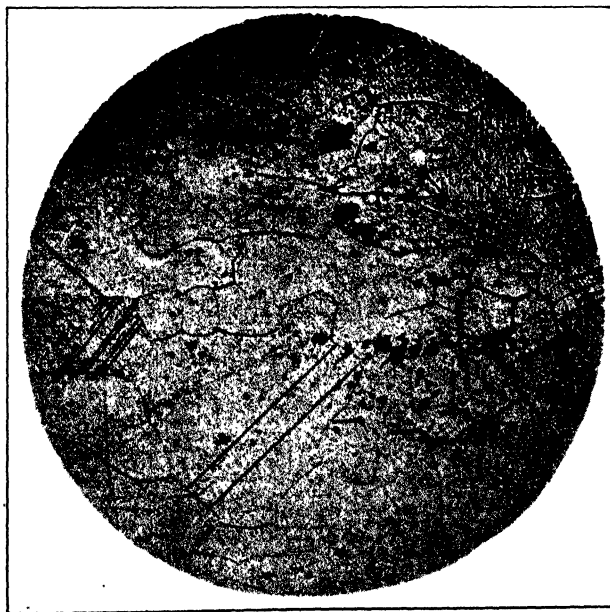


FIG. 20.—POSITION 1 OF SPECIMEN 8; 128-MM. AIR SPACE BETWEEN SPECIMEN AND EXPLOSIVE. $\times 200$.



FIG. 21.—POSITION 2 OF SPECIMEN 8; 128-MM. AIR SPACE BETWEEN SPECIMEN AND EXPLOSIVE. $\times 200$.

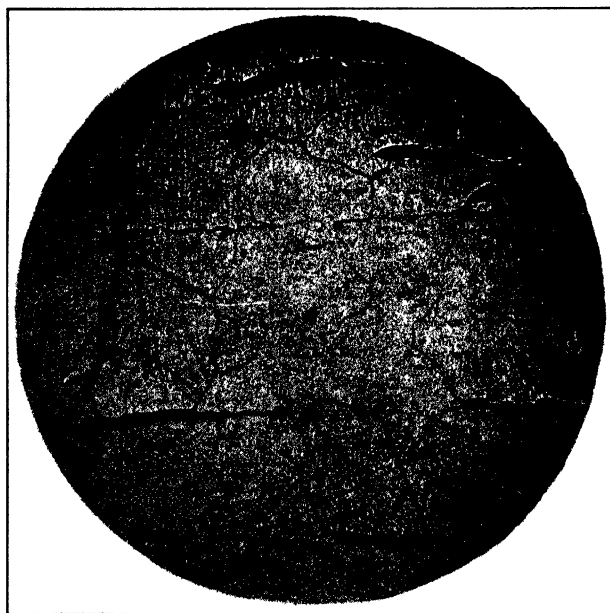


FIG. 22.—POSITION 3 OF SPECIMEN 8; 128-MM. AIR SPACE BETWEEN SPECIMEN AND EXPLOSIVE. $\times 200$.

A sensitive test of the solution after removal of the pieces showed no trace of copper. This is a point in favor of the use of copper as a coating and hydrochloric acid as a solvent. The disadvantage of using a copper coating is that it readily oxidizes on the surface when exposed to the air and probably there is some gain in weight from this source. Nevertheless, the results obtained by weighing agree better within themselves than do the losses obtained by titration. Evidently a better method of analyzing for such small amounts of iron will have to be adopted.

There was a negligible loss in weight after $\frac{1}{2}$ hr. in the acid. A general agreement exists between the weight loss and titration loss found after 1 hr. in the solution, Fig. 23. In both the $\frac{1}{2}$ and 1-hr. tests the loss by titration is greater than that found by weighing. When it is consid-

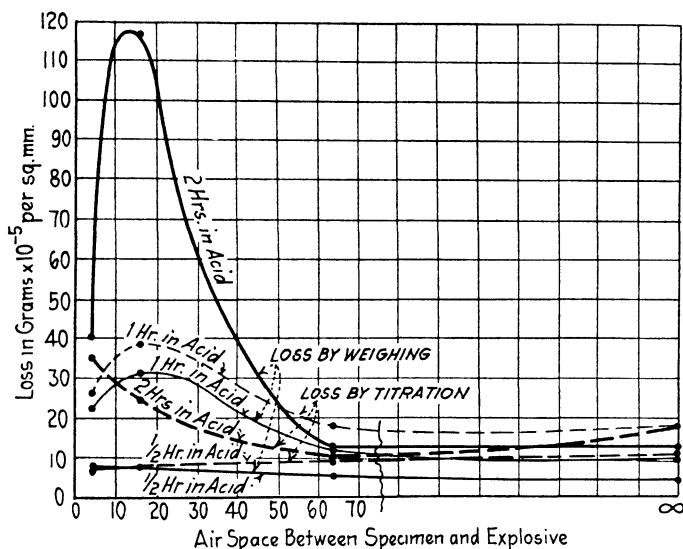


FIG. 23.—SOLUBILITY IN HYDROCHLORIC ACID.

ered that the weight loss takes in the loss from the solution of other elements than iron and that the titration loss represents only the iron dissolved, the loss determined by weighing should be greater rather than less, than the loss determined by titration. Only in the 2-hr. test does the titration loss appear less than that obtained by weighing, but here the titration loss is less in 2 hr. than that found after a 1-hr. test. This throws the analytical method under suspicion. In general, we do not feel that much weight can be given the quantitative values obtained and we do not feel justified in making a comparison on that basis. Specimens 2, 4, 6, and 8 air gap have been held back for solubility tests after our methods of determining solubility have been improved. Improvement should be made in the method of analyzing our solution for iron after removal of the pieces. The results obtained warrant us in going forward with the determination of solubility.

DISCUSSION

B. STOUGHTON, Bethlehem, Pa.—Mr. Foley, did you use a standard in connection with this solubility? For example, we know that acid steel dissolves more slowly in dilute acids than basic steel. You would have to have some base line to start from in determining the Neumann bands in relation to the solubility.

F. B. FOLEY.—Our standard for determination of the effect of Neumann bands on solubility has been a specimen free of Neumann bands before subjecting it to impact. We used no other standard.

S. L. HOYT, Schenectady, N. Y.—By their recent studies of the production of Neumann bands and by the use of a new type of ocular, Dr. Rosenhein and Dr. McMeekan were able to obtain results in a microscopic study such as this which hitherto had not been produced, and their evidence showed fairly conclusively, and certainly to Dr. Rosenhein's own personal satisfaction, that Neumann bands were not twins. On the other hand, the band, when studied with this new means, was shown to consist of a series of more or less roughly parallel lines, not at all a homogeneous band; secondly, slip lines subsequently produced on a sample which had already been subjected to impact and polished to show Neumann bands, showed that the slip band did not cross the Neumann bands with the same structure which you would get, for example, in a piece of twinned copper. In other words, the slip bands in crossing the Neumann band ran at random orientation with respect to the band proper. If the Neumann band were a twin we would have reason to expect perfect parallelism of these slip bands.

Mr. Foley, did you consider the nature of Neumann bands in the light of Dr. Rosenhein's recent contribution, and did you find yourself in agreement therewith?

F. B. FOLEY.—My recollection is that Rosenhein said that with the velocities used he did not think the Neumann bands were twins, but he did not know about any higher velocity such as we had used in our work here. The best evidence of twinning I have obtained is in one particularly good photomicrograph at 930 diameters in an earlier paper.⁵ There it is shown that Neumann bands are not only depressions but also elevations. In other words, in one crystal a Neumann band appears as a mountain or ridge and in another as a trough or trench.

I imagine that the reason why a Neumann band will appear in this particular crystal as a trench and in another as a prominence or ridge is due to the difference in the solubility of the faces presented to the acid during the acid attack. That is, if an 001 cube face is presented to the

⁵ *Trans.* 48, 912, Fig. 39.

acid that face is attacked much less rapidly than an octahedral, 111 plane face would be.

These considerations satisfy my own personal conception of twinning in a solid crystal. I am not referring to interpenetrating twins which form from the liquid, in which case one crystal appears to pass through another. These are two conditions which are quite different—I imagine the twin in solid crystal formed by impact has to be considered as something different from the congenital twin produced from a liquid solution.

C. P. YAP,* New York, N. Y.—For some time I have been most interested in Neumann bands. About a year ago I had an interesting experiment with a piece of Armco iron. I thought that if Neumann bands are twinning planes, twinning may reasonably be expected to take place under compression. On the other hand, if they are slip bands or mechanical cleavages, they may be expected to be present as a result of tensional stress. The piece was carefully polished and examined to see

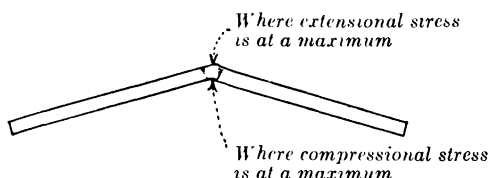


FIG. 24.—SPECIMEN OF ARMCO IRON PREPARED FOR EXAMINATION FOR NEUMANN BANDS.

if any Neumann bands were present, but very few were visible. Then with a vise and hammer, I bent it by quick blows to about an angle of 90° . I had the specimen prepared for microscopic examination, at *A* and *B* (Fig. 24) where the compressional and extensional stress are greatest. There were numerous Neumann bands at *B* and hardly any at *A*. Moreover, these bands have appreciable width.

F. B. FOLEY.—I cannot see why twins could not be produced in tension as well as in compression. Do you know that it is not possible to produce them by tension?

C. P. YAP.—My knowledge of this subject is rather limited, but I would expect twinning to result from compressional stresses, as illustrated by the formation of twinned martensitic needles. Three years ago in a lecture at the Rice Institute of Houston, Texas, Prof. Miers stated that twinning is not extensive in rapid crystallization, whereas it is extensively found in case of slow crystallization when the stresses are more or less uniformly distributed throughout the mass of the cooling body. But then the mechanism of twinning in iron may be entirely under different conditions.

* Research Assistant to Dr. Ancel St. John.

J. S. VANICK, Bayonne, N. J.—There is a distinguishing characteristic in Neumann bands in alpha iron, that I think Mr. Foley has not enlarged on, and that is the ragged band they form, but which you do not find in the same bands in gamma or in the brasses. These micrographs show this feature and I have come across it many times in examining similar structures. The explanation, as near as I can see, lies in the ultimate crystal structure of the two; that is, the body-centered form of the alpha and the face-centered lattice pattern for the gamma and brasses give two different sets of gliding planes for the deformation to act upon. In the gamma grains or in the face-centered lattices the bands are parallel, straight-sided and usually stop within the grain and are more of the nature of block movements. In the alpha grains they are frequently irregular, cross-grain boundaries and run the entire length of the specimen. That is especially well shown in the meteorites.

F. B. FOLEY.—This type of Neumann band was well illustrated in one of Dr. Krivobok's slides.⁶ It occurred to me that the twinning planes were approaching the surface at an angle, where they gave a nodal effect with saw edges, similar to that produced when the lamellae in pearlite approached the surface of the specimen at an angle as shown in photographs taken by Belaiew and which he used for measuring the width of the pearlite lamellae. I am curious to know if the nodal effect is not caused by the angle which the twin makes with the surface of the specimen. I notice on one side of the bands the line is perfectly straight and on the other side it is jagged.

J. S. VANICK.—That was the pattern I had always associated with Neumann bands. The other straight-line patterns, also interpreted as slip bands or twinning bands, depend on whether the structure has been heated or cooled.

G. ST. J. PERROTT,* Pittsburgh, Pa. (written discussion).—In experiments recently carried out at the Explosives Testing Station of the Bureau of Mines, Bruceton, Pa., it has been shown that the velocity of the shock wave across a 6-in., air gap between two cartridges of 40 per cent. straight nitroglycerin dynamite wrapped in a paper tube is only 400 m. per sec. less than the rate of detonation of the explosive. It is, therefore, evident that decrease in the magnitude of the blow rather than in its velocity was responsible for the decrease in the number of Neumann bands in the author's experiments as the air gap between explosive and specimen was increased.

F. B. FOLEY (written reply to discussion).—The 40 per cent. straight nitroglycerin dynamite which Dr. Perrott used would have a rate of

⁶A. I. M. E. Pamphlet No. 1557-E., issued with MINING AND METALLURGY, Feb., 1926.

* Assistant chief explosives chemist, Bureau of Mines Experiment Station.

detonation in a $1\frac{1}{4}$ -in. diameter cartridge of 4470 m. per sec. A loss of but 400 m. per sec. in velocity in 6 in. would still leave a high rate of velocity at the greatest distance (128 mm.) intervening between the explosive and any of the specimens used in our experiment. Velocities as low as 1523 m. per sec. were sufficient to produce Neumann bands in our previous work in which the explosive was directly in contact with the specimens. It, therefore, seems obvious that, as Dr. Perrott says, the decrease in energy is responsible for the decrease in the number of Neumann bands. Still, to produce them at all in this material, a certain, but unknown, rate of application seems necessary—a very slow rate of application of large amount of energy giving rise to slip bands and general deformation. Apparently in relatively brittle, coarse-grained irons Neumann bands may be produced by mere static deformation and as the material becomes finer grained high velocities of application of energy seem to be necessary and possibly when a certain fineness of grain is attained Neumann bands may not form at all. Grain size, mass and velocity are the factors involved.

The Iron-tungsten System

By W. P. SYKES,* CLEVELAND, OHIO

(New York Meeting, February, 1926)

IN CONNECTION with a study of tungsten steels, Honda and Murakami¹ reported an investigation of the system iron-tungsten. This report included a tentative equilibrium diagram, photomicrographs of various alloys in the series, and qualitative measurements of hardness and magnetic properties. The present investigation originally had as its object the study of the hardness and tensile properties of a series of carbon-free iron-tungsten alloys. But, as the work progressed it became evident that the system possessed other features of interest, so the scope of the investigation was enlarged.

MATERIALS

The iron powder used in preparing the alloys was obtained as follows: Iron oxalate was precipitated from a ferrous-sulfate solution by the addition of a solution of oxalic acid. This oxalate, after thorough washing, was ignited to iron oxide, which after reduction in hydrogen at about 1000° C. yielded iron powder containing but about 0.2 per cent. iron oxide and about 0.005 per cent. carbon. Tungsten metal in the form of powder, such as is used in the manufacture of filaments for incandescent lamps, was the other constituent. This material analyzed 99.8 per cent. tungsten and contained no carbon. The metal powders, in the desired proportions, were mixed by tumbling and formed, under pressure of 20 tons per sq. in., into rods $\frac{3}{8}$ by $\frac{3}{8}$ by 10 in.

To form the alloys without contamination, sections of the pressed rods were placed on alundum slabs and heated in an alundum tube wound with a tungsten resistor and packed in heat-insulating material. While the resistor was heated, a stream of hydrogen was continually passed through both the tube and the case containing it. The tungsten winding on the tube, as well as the material heated within the tube, was thus protected from oxidation. Such a furnace will operate constantly for several days at temperatures up to 1500° C. and for shorter periods

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¹ Kotara Honda and K. Murakami: *Sci. Rep. Tohoku Imp. Univ.*, **6**, No. 5.

when the temperature is raised to 1800°C . At this temperature, the alundum softens and the tube collapses after a few hours.

In this furnace complete fusions were made of iron tungsten alloys containing tungsten up to 60 per cent. To fuse completely an alloy richer in tungsten than 60 per cent., it was necessary to heat the pressed rod directly by passing current through it, the rod being mounted between water-cooled electrodes and protected from oxidation by an atmosphere of hydrogen.

TEMPERATURE DETERMINATIONS

As the lowest melting point in the series is about 1525°C . the general use of a thermocouple is accompanied by serious difficulties. Most of the

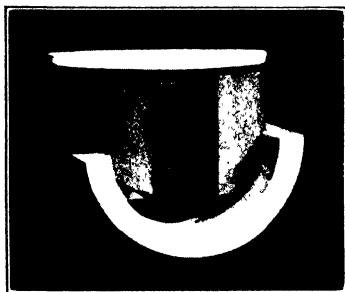


FIG. 1.—ALUNDUM HOOD CONTAINING SPECIMEN FOR DETERMINATION OF FUSION TEMPERATURE WITH OPTICAL PYROMETER.

temperature measurements above 1500°C . were made with an optical pyrometer. A block of the metal to be fused was placed on a section of alundum tubing; over this block was set an alundum hood with a section removed through which the pyrometer could be sighted on the inside wall, just behind and above the specimen, as shown in Fig. 1. The specimen, thus mounted, was placed in the furnace at approximately 1450°C . and the temperature increased at the rate of about 1°C . per minute. The first liquid formed appears in sharply defined black spots on the surface, or more often black lines on the edges of the block of metal. This dark area is presumably the reflection of the relatively dark open end of the furnace tube.

Several such determinations of the melting point of pure iron were in agreement, within $\pm 3^{\circ}\text{C}$. The fusion temperature of pure nickel under like conditions was also noted. From these readings a slight correction was applied to the calibration chart of the pyrometer lamp. The alloys used for fusion-temperature determinations were previously heated for several hours at 1500°C . to 1515°C ., to insure thorough diffusion of the components. By following this procedure, the observed temperatures

at which fusion commenced for a given composition agreed as closely as the corresponding readings taken on pure iron.

When plotting these temperatures, the first appearance of fusion was taken as the solidus. The liquidus, or temperature of complete fusion, was less definitely marked. However, by raising the temperature through the fusion range at a rate as low as 10° C. per hr. and noting the point at which the melt assumed a convex surface, the liquidus could be fixed within, say $\pm 5^{\circ}$ C. These determinations were supplemented by microscopic examinations of the specimen, in which any unfused material could be identified.

In the range between 40 and 50 per cent. tungsten, a thermocouple was immersed in the melt and a cooling curve taken to determine, as accurately as possible, the location of the eutectic, which was indicated by the optical pyrometer readings and the microstructure.

EQUILIBRIUM DIAGRAM

The equilibrium diagram of the system iron-tungsten arrived at by fusion-point determinations and microscopic examination of alloys of the

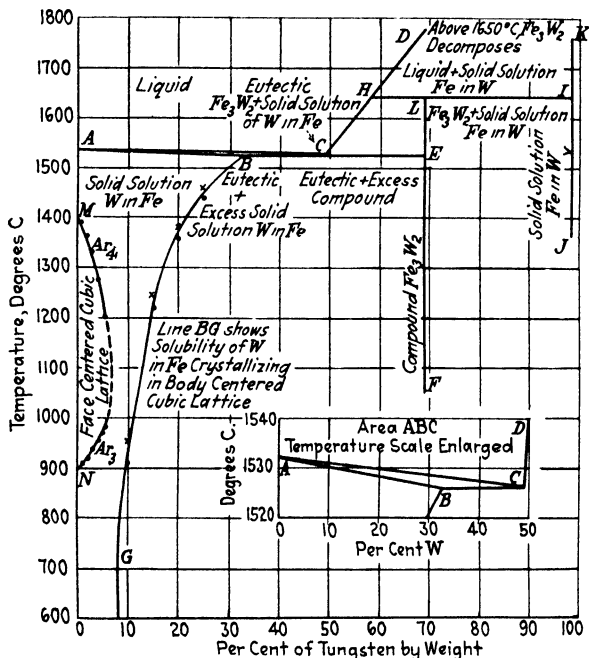


FIG. 2.—PART OF EQUILIBRIUM DIAGRAM OF IRON-TUNGSTEN SYSTEM.

system is shown in Figs. 2 and 3. At 1525° C., iron will hold in solid solution about 33 per cent. by weight of tungsten and the melting point of this composition is less than 10° C. below that of pure iron.

Iron-tungsten alloys containing 33 per cent. or less of tungsten when quenched from the solidus will present, under the microscope, only the large polyhedral grains of the solid solution, Fig. 4. The range from pure iron to 6 per cent. tungsten offers some peculiar features of microstructure, which will be described later.

When an alloy of iron and 33 per cent. or less of tungsten is cooled from fusion to room temperature over a period of several hours, a second phase appears as a precipitate somewhat crystalline in form and unattacked by a nitric-acid etch. It appears first at the grain boundaries.

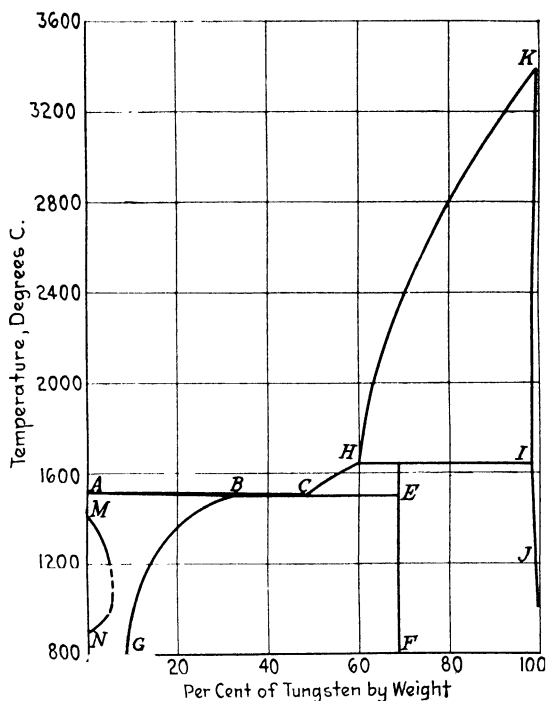


FIG. 3.—EQUILIBRIUM DIAGRAM OF IRON-TUNGSTEN SYSTEM.

With slower cooling or lengthy heating at some temperature near 1200° C., this phase is scattered throughout the grains of solid solution; see Fig. 5. This second phase appears to be the compound Fe_3W_2 containing 68.7 per cent. tungsten, which is found to be the single constituent of an alloy of that composition after prolonged heating at 1550° to 1575° C. This compound has been given the name iron tungstide,² but its composition had been placed at 62 per cent. tungsten, or the compound Fe_2W .

On slow cooling, then, the tungsten, in the form of the iron tungstide, precipitates in the solid along the line BG, Fig. 2. This line was located by microscopic examination of a series of specimens, water-quenched

²H. Harkort: Metall., (1907) 18, 19, 20.

after heating for 6-hr. periods at temperatures ranging between 700° and 1500° C. As an example may be cited the determination of solid solubility temperature of 20 per cent. tungsten in iron. Several blocks of the alloy of this composition were prepared by heating at 1500° C. for 6 hr., and water-quenched. Their microstructure was that of the solid solution—the single phase. One specimen was replaced in the furnace at 1500° C., the temperature lowered to 1450° C. and held within 10° C. of that temperature for 6 hr. The specimen was then water-quenched and its microstructure noted. As none of the second phase was visible, a



FIG. 4.—TUNGSTEN 30 PER CENT., IRON 70 PER CENT., WATER-QUENCHED FROM 1500° C.; ETCHED WITH 10 PER CENT. NITRIC ACID IN ALCOHOL. $\times 1000$.

second block of this alloy was cooled to 1400° C., held at that temperature 6-hr., quenched and examined. A piece held at 1350° C., was the first of this composition to show any precipitate of the tungstide. By further heatings at 1360° and 1380° C., the point on the solid-solubility curve for this alloy was placed at 1370° C.

The tungstide precipitated at temperatures of 700° or 800° C. can be easily discerned by the rapid darkening of the surface of the alloy when immersed in 10 per cent. nitric-acid etching solution. The alloy containing 8 per cent. tungsten after holding for 6 hr. at 600° C. showed no indications of a precipitate. This percentage then was taken as the solid solubility of tungsten in iron at 600° C. Specimens of 8 per cent. tungsten content held at 500° C. for 40 or 60 hr. failed to develop any indications of a precipitate.

With an increase in tungsten above 33 per cent., the tungstide appears in specimens quenched from the solidus. The alloy 49 per cent. tungsten-

51 per cent. iron appears to be a eutectic. The freezing point of this alloy, as determined by the thermocouple, is 1527°C .; by the optical

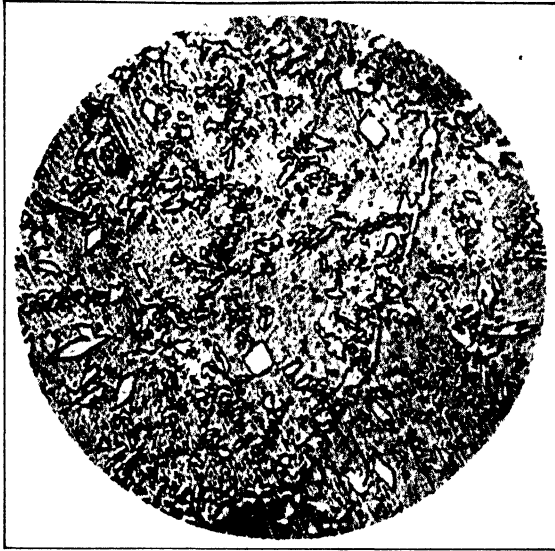


FIG. 5.—TUNGSTEN 30 PER CENT, IRON 70 PER CENT, FURNACE-COOLED, IN 40 HR. FROM 1500° TO 500°C . $\times 500$.

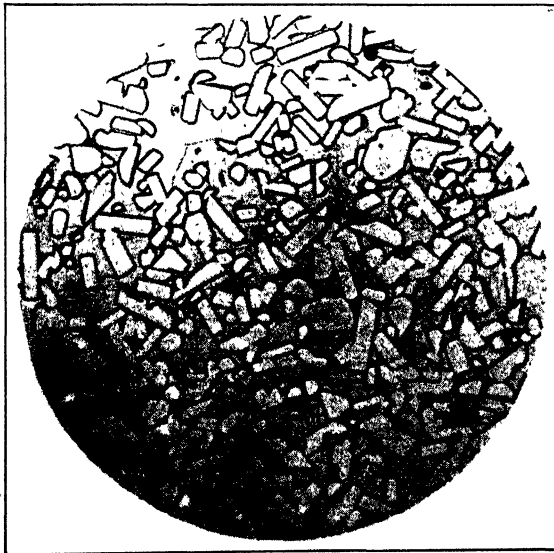


FIG. 6.—TUNGSTEN 49 PER CENT, IRON 51 PER CENT., FUSED, FURNACE-COOLED TO ABOUT 1520°C . AND QUENCHED; EUTECTIC COMPOSITION. $\times 100$.

pyrometer, this temperature was determined as 1525°C . The alloy fuses at a constant temperature, the lowest observed in the series, and

presents a characteristic microstructure, apparently a conglomerate of imperfectly formed crystals of iron tungstide mixed with a definite percentage of the solid solution of tungsten in iron. This structure is illustrated in Fig. 6. As the tungsten content increases from 33 to 49 per cent., this eutectic-like structure occupies increasingly more of the total area of the cross-section. In the alloy shown in Fig. 7, containing 35 per cent. tungsten, a small amount of the eutectic appears near the edge of the section. The long needles of the compound were precipitated in the excess solid solution along the line *BG*, Fig. 2, as the alloy cooled below the solidus to 1500° C., at which temperature this specimen was quenched.

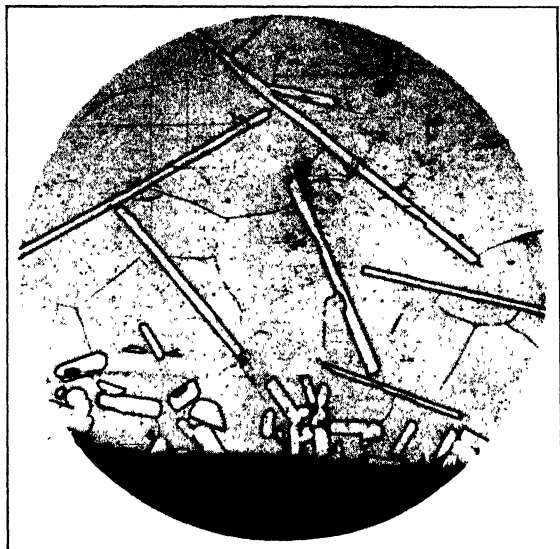


FIG. 7.—TUNGSTEN 35 PER CENT., IRON 65 PER CENT., FUSED, FURNACE-COOLED TO ABOUT 1500° C. AND QUENCHED. $\times 100$.

In the alloy containing 45 per cent. tungsten, Fig. 8, the eutectic actually takes up the greater part of the section. The photomicrograph was taken at the border of the eutectic and excess solid solution.

As indicated by the line *BE*, Fig. 2, the first indications of fusion occur at 1525° C. in all the compositions between 33 and 68 per cent. tungsten. Increasing the tungsten content above 49 per cent. results in the formation of larger masses of Fe_3W_2 and a rapid rise in the liquidus line *CH*. The alloy of 55 per cent. tungsten, 45 per cent. iron, shown in Fig. 9, did not completely fuse until the temperature reached 1600° C.

By prolonged heating below the liquidus, the compound Fe_3W_2 can be formed in amounts that increase with the tungsten content. In Fig. 10, is shown a section of the 62 per cent. tungsten alloy after heating for 20 hr. at 1550°–1575° C. It is composed of large areas of iron tungstide inclosing patches of the eutectic or iron-rich portion of the eutectic,

During the formation of the compound at temperatures near 1550°C ., there is considerable shrinkage which results in the formation of many

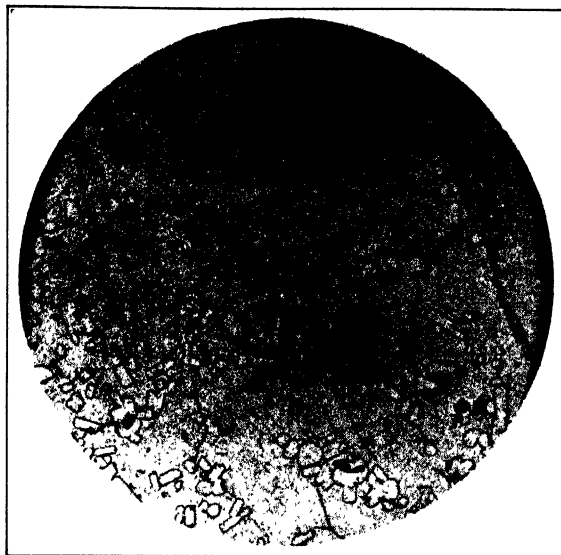


FIG. 8.—TUNGSTEN 45 PER CENT., IRON 55 PER CENT.; FUSED, FURNACE-COOLED TO ABOUT 1520°C . AND QUENCHED. $\times 100$.

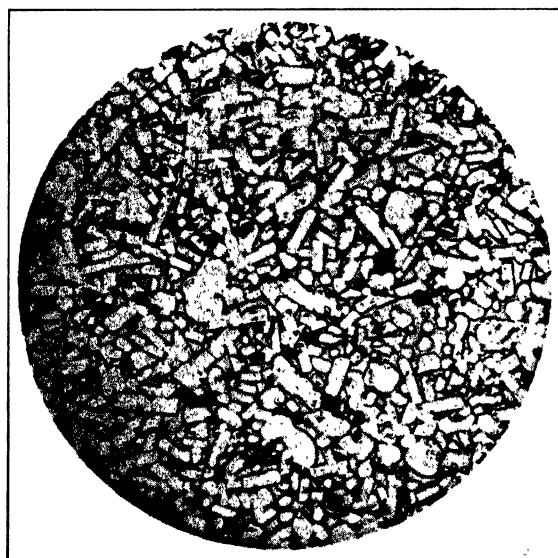


FIG. 9.—TUNGSTEN 55 PER CENT., IRON 45 PER CENT.; FUSED, FURNACE-COOLED TO ABOUT 1520°C . AND QUENCHED. $\times 100$.

voids throughout the material. The alloy after heating for 30 hr. at 1550° – 1575°C . is shown in Fig. 11. As far as can be observed, it is made

up of only one phase. The large black patches are the shrinkage cavities; small black etching pits are visible throughout the compound. Electro-



FIG. 10.—TUNGSTEN 62 PER CENT., IRON 38 PER CENT.; HEATED 20 HR. 1550° TO 1575° C. QUENCHED. $\times 300$.

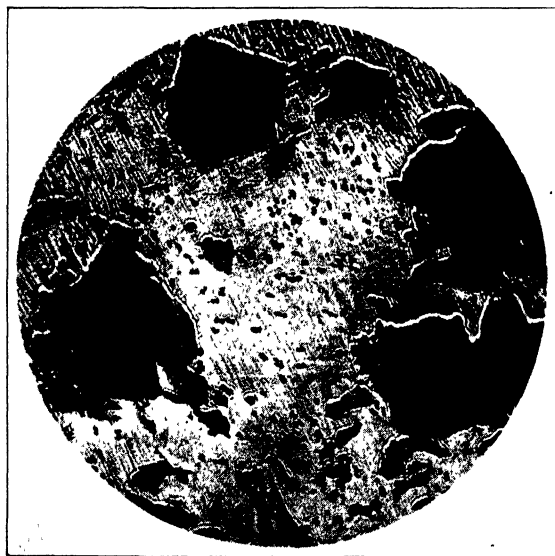


FIG. 11.—TUNGSTEN, 69 PER CENT., IRON 31 PER CENT., THE COMPOUND Fe_3W_2 FORMED DURING 30 HR. HEATING AT 1550° TO 1575° C. $\times 300$.

lytic etching in a solution of sodium hydroxide will develop faint grain boundaries in the compound.

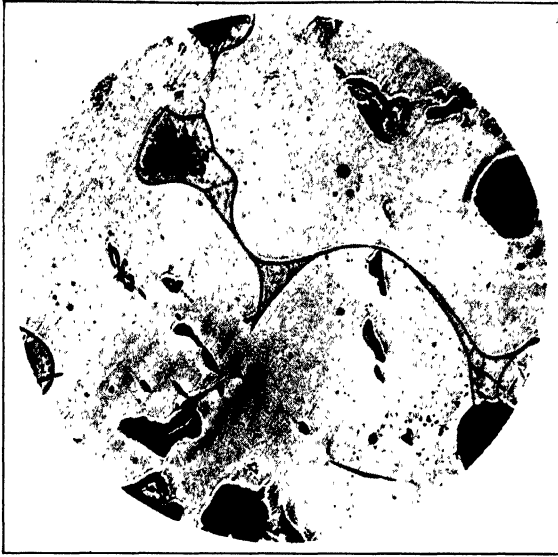


FIG. 12.—TUNGSTEN 69 PER CENT., IRON 31 PER CENT.; INCOMPLETE FORMATION OF Fe_3W_2 DURING 20 HR. HEATING AT 1550° TO 1575°C. ; SMALL AREAS OF IRON-RICH MATERIAL SURROUNDED BY UNETCHED TUNGSTIDE. $\times 300$.



FIG. 13.—TUNGSTEN 69 PER CENT., IRON 31 PER CENT.; AFTER COMPLETE FORMATION OF COMPOUND THIS SPECIMEN WAS HEATED TO 1700°C. AND Fe_3W_2 PARTLY DECOMPOSED. THREE PHASES: 1, TUNGSTEN RICH; 2, IRON TUNGSTIDE; 3, IRON RICH. $\times 1000$.

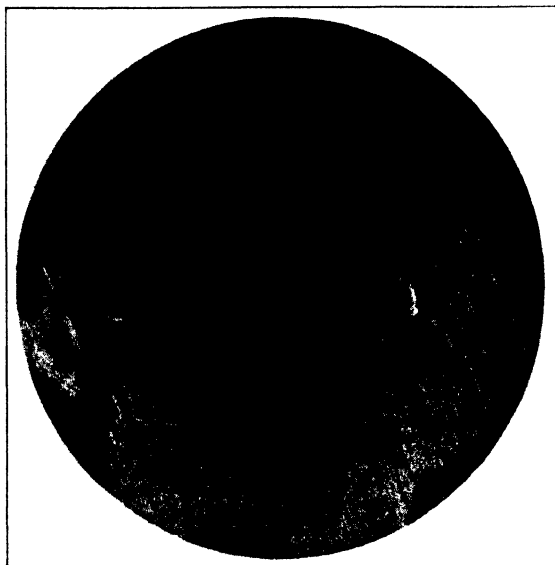


FIG. 14.—SAME SPECIMEN AS IN FIG. 13; AFTER HEATING $\frac{1}{2}$ HR. AT ABOUT 1550° C. SHOWS Fe_3W_2 INCREASING IN AMOUNT. THREE PHASES: 1, TUNGSTEN RICH; 2, IRON TUNGSTIDE; 3, IRON RICH. $\times 1000$.



FIG. 15.—SAME SPECIMEN AS IN FIGS. 13 AND 14; AFTER HEATING 3 HR. AT 1550° C. COMPOUND Fe_3W_2 HAS BEEN FORMED AGAIN ALMOST COMPLETELY. TWO PHASES: 1, TUNGSTEN RICH; 2, IRON TUNGSTIDE. $\times 1000$.



FIG. 16.—TUNGSTEN 65 PER CENT., IRON 35 PER CENT.; AFTER HEATING 1 HR. AT 1650° C. DECOMPOSITION OF TUNGSTIDE HAS BEGUN. 1, TUNGSTEN RICH; 2, TUNGSTIDE Fe_3W_2 ; 3, IRON RICH. $\times 500$.

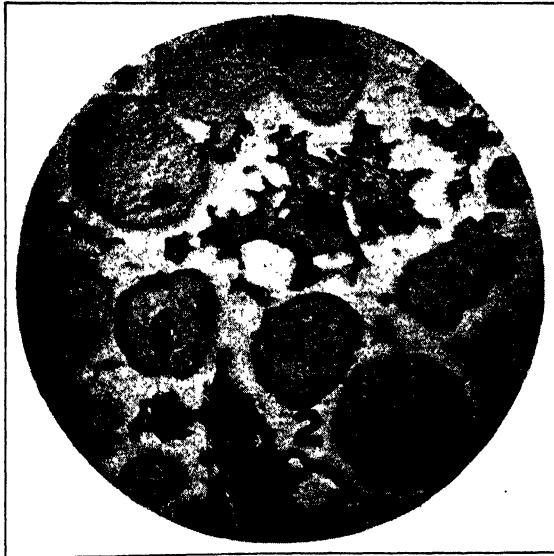


FIG. 17.—TUNGSTEN 75 PER CENT., IRON 25 PER CENT.; HEATED 6 HR. AT 1675° C. AND QUENCHED; SHOWS PARTIAL DECOMPOSITION OF TUNGSTIDE. THREE PHASES: 1, TUNGSTEN RICH; 2, IRON TUNGSTIDE; 3, IRON RICH. $\times 1000$.

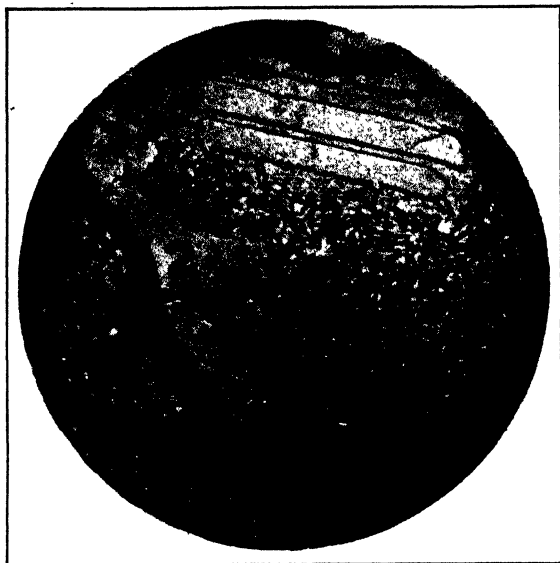


FIG. 18.—TUNGSTEN 62 PER CENT., IRON 38 PER CENT.; COOLED SLOWLY FROM 1675° C. 1, TUNGSTEN RICH; 2, IRON TUNGSTIDE; 3, IRON-RICH SOLID SOLUTION FROM WHICH PARTICLES OF TUNGSTIDE HAVE PRECIPITATED. $\times 1000$.



FIG. 19.—TUNGSTEN 75 PER CENT., IRON 25 PER CENT.; HEATED 20 HR. 1550° TO 1575° C.; TUNGSTEN-RICH PHASE IN CENTER OF FIELD, SURROUNDED BY IRON TUNGSTIDE. $\times 1000$.



FIG. 20.—TUNGSTEN 85 PER CENT., IRON 15 PER CENT.; HEATED 20 HR. 1550° TO 1575° C.; ROUNDED AREAS OF TUNGSTEN-RICH PHASE SURROUNDED BY Fe_3W_2 . $\times 500$.

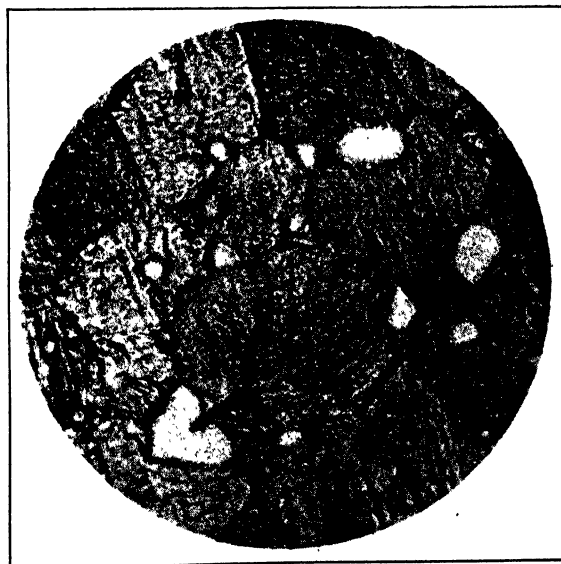


FIG. 21.—TUNGSTEN 98.5 PER CENT., IRON 1.5 PER CENT.; HEATED 20 HR. AT 1600° TO 1625° C.; WHITE AREAS OF Fe_3W_2 IN TUNGSTEN-RICH MATRIX. $\times 1000$.

This composition is the first of the series to show no attraction for the compass needle, and this is brought about only after heating for 25 to 30 hr. at about 1550° C.

If an alloy containing more than 60 per cent. of tungsten is heated to 1650° C. or above, a decomposition of the compound sets in. This fact is denoted by line *HL*, Fig. 2. Within the tungstide appears a tungsten-rich area 1, Figs. 13, 16, and 17, and outside the tungstide is a phase that seems to be the solution of tungsten in iron. In Fig. 18, this iron-rich area 3 is covered with small particles of the tungstide, which probably were precipitated in accordance with the equilibrium as shown by line *BG*, Fig. 2.

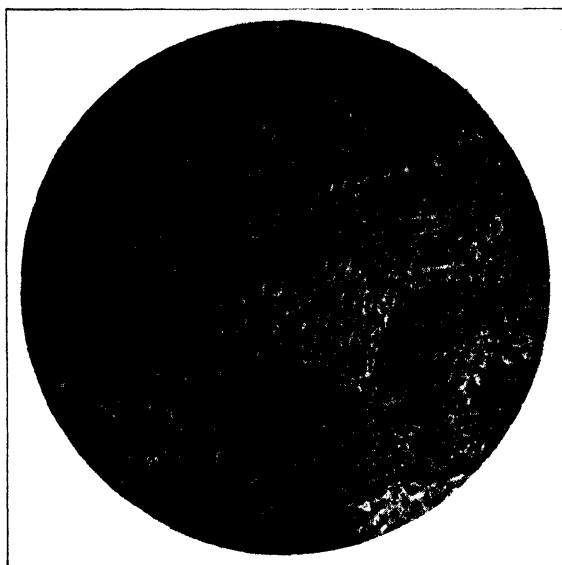


FIG. 22.—TUNGSTEN 99 PER CENT., IRON 1.0 PER CENT.; HEATED 20 HR. AT 1600° TO 1625° C. $\times 1000$.

By heating again, at a lower temperature, an alloy in which the tungstide has been decomposed, the compound can be to a large extent reformed; see Figs. 14 and 15. The decomposition occurring at temperatures above 1650° C. is accompanied by the reappearance of magnetic properties in the alloy; this fact indicates that free iron is one of the products of the composition.

A tungsten-rich phase appears and increases in quantity as the tungsten content is raised. In alloys formed below 1650° C., this tungsten-rich material occurs in the form of islands surrounded by the tungstide; see Figs. 19 and 20. At the tungsten-rich end of the diagram, this solubility of iron in tungsten at 1600° C., as determined by examination of a series of alloys, was placed at 1.20 per cent. Tungsten contain-

ing 1.50 per cent. iron, after 12 hr. heating at $1600^{\circ}\text{C}.$, shows some undissolved iron present as the iron tungstide, Fig. 21.

The solid solution of 1 per cent. iron in tungsten as quenched, after heating 12 hr. at $1600^{\circ}\text{C}.$, is shown in Fig. 22. If this alloy is gradually heated to fusion by an electric current, the section at which fusion occurs will show segregations of iron-rich material in the form of envelopes surrounding the tungsten-rich grains; see Fig. 23. This shows that iron lowers the freezing point of tungsten very markedly, as shown by the solidus line *KI*, Fig. 3. Alloys containing from 69 to 95 per cent. tungsten were fused in this same manner. No attempt was made to determine the temperatures at which complete fusion occurred, but as no new phases

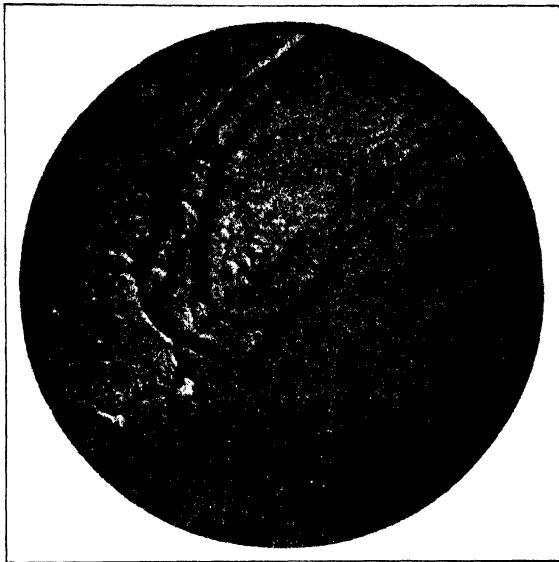


FIG. 23.—TUNGSTEN 99 PER CENT., IRON 1 PER CENT.; HEATED 20 HR. AT $1600^{\circ}\text{C}.$ THEN FUSED; SHOWS ENVELOPES OF IRON-RICH MATERIAL AROUND GRAINS OF TUNGSTEN-RICH PHASE. $\times 1000$.

were noticeable in the microstructure, the liquidus line *KH*, as drawn, should be representative of this part of the diagram.

CRITICAL POINTS

When alloys containing 5 per cent. and less of tungsten were first examined some irregularities were noted. For example, the alloy of 5 per cent. tungsten-95 per cent. iron showed a decidedly higher hardness when water-quenched from $1500^{\circ}\text{C}.$ than when furnace cooled; but no measurable difference in hardness could be detected between quenched and slowly cooled blocks of the 10 per cent. tungsten alloy. Likewise, the 5 per cent. alloy exhibited a marked refinement in grain size in the

quenched condition, which was not found in any specimen of higher tungsten content observed up to that time. This grain refinement and hardness increase brought about by a water quench from elevated temperatures had been noted in the pure iron, but to a much less marked degree. These findings suggested the possibility of some change in the position of the A_3 critical point of iron by the addition of small amounts of tungsten.

A series of alloys of iron with tungsten content increasing by 1 per cent intervals from 1 to 6 per cent. was prepared for thermal analysis. These specimens were in the form of blocks about 1 by 1 by 3 in. each, weighing about 250 gm., and, after drilling for the insertion of the thermocouple,

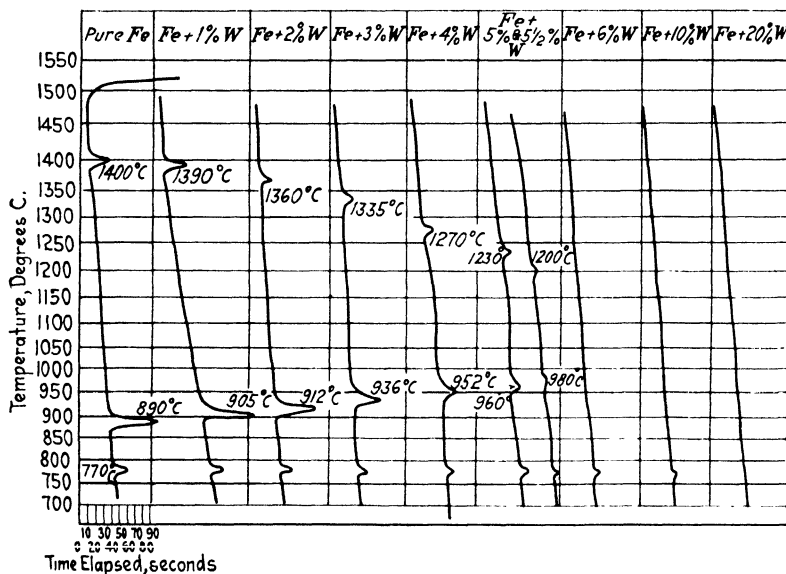


FIG. 24.—COOLING CURVES OF IRON-TUNGSTEN ALLOYS.

were heated at 1500° C. for 2 hr. A platinum-platinum rhodium couple calibrated by the melting points of pure copper, nickel, and iron was inserted in the specimen in a thin-walled silica tube and the furnace allowed to cool from 1500° to about 500° C. The furnace used was similar to that heretofore described. After the couple had been placed in the specimen, the flow of hydrogen into the furnace was reduced and the end of the furnace tube was packed with asbestos. The temperature of the cooling specimen was followed with a galvanometer and potentiometer, readings being taken at intervals of 0.10 millivolt.

The inverse rate cooling curves are plotted in Fig. 24 for pure iron and iron containing tungsten in amounts from 1 to 20 per cent. In the cooling curve for pure iron, which was started from the fusion temperature, the three critical points are strongly pronounced at 1400°, 890° and 770° C. With increase in tungsten content, the temperature of the Ar_4 point is

rapidly lowered while that of the Ar_3 point is less rapidly raised. When the tungsten content has reached 5.5 per cent., both points are barely noticeable, Ar_4 at 1200° and Ar_3 at 980° C. The position of Ar_2 remains unchanged and can still be detected in the 20 per cent. tungsten alloy. The cooling rate of the furnace and specimens in these determinations decreased from 18° C. per min., at the high temperatures, to about 12° per min. at 700° C.

TABLE 1.—*Temperatures of Maximum Time Intervals for Ar_4 and Ar_3 Points*

Specimen	Maximum Temperature, Degrees C.	
	Ar_4	Ar_3
Pure Fe	1400	890
Fe + 1% W.	1390	905
Fe + 2% W.	1360	912
Fe + 3% W.	1335	936
Fe + 4% W.	1270	952
Fe + 5% W.	1230	960
Fe + 5.5% W.	1200	980

Cooling rate 18° C. to 15° C. per min.

Cooled from 1500° C.

In Table 1 are listed the temperatures of maximum time intervals for both points in pure iron and in the iron-tungsten series as observed

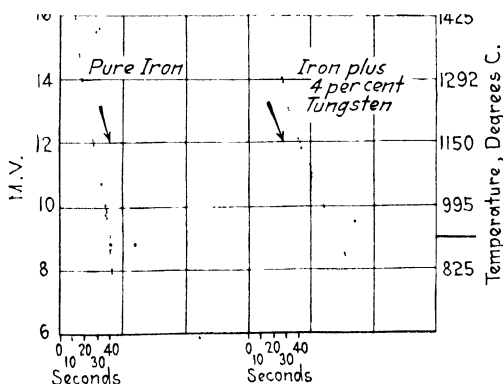


FIG. 25.—MILLIVOLTMETER AND TEMPERATURE READINGS OF PURE IRON AND IRON PLUS 4 PER CENT. TUNGSTEN.

under these conditions of cooling. For each composition two, and in some cases three, separate sets of observations were made.

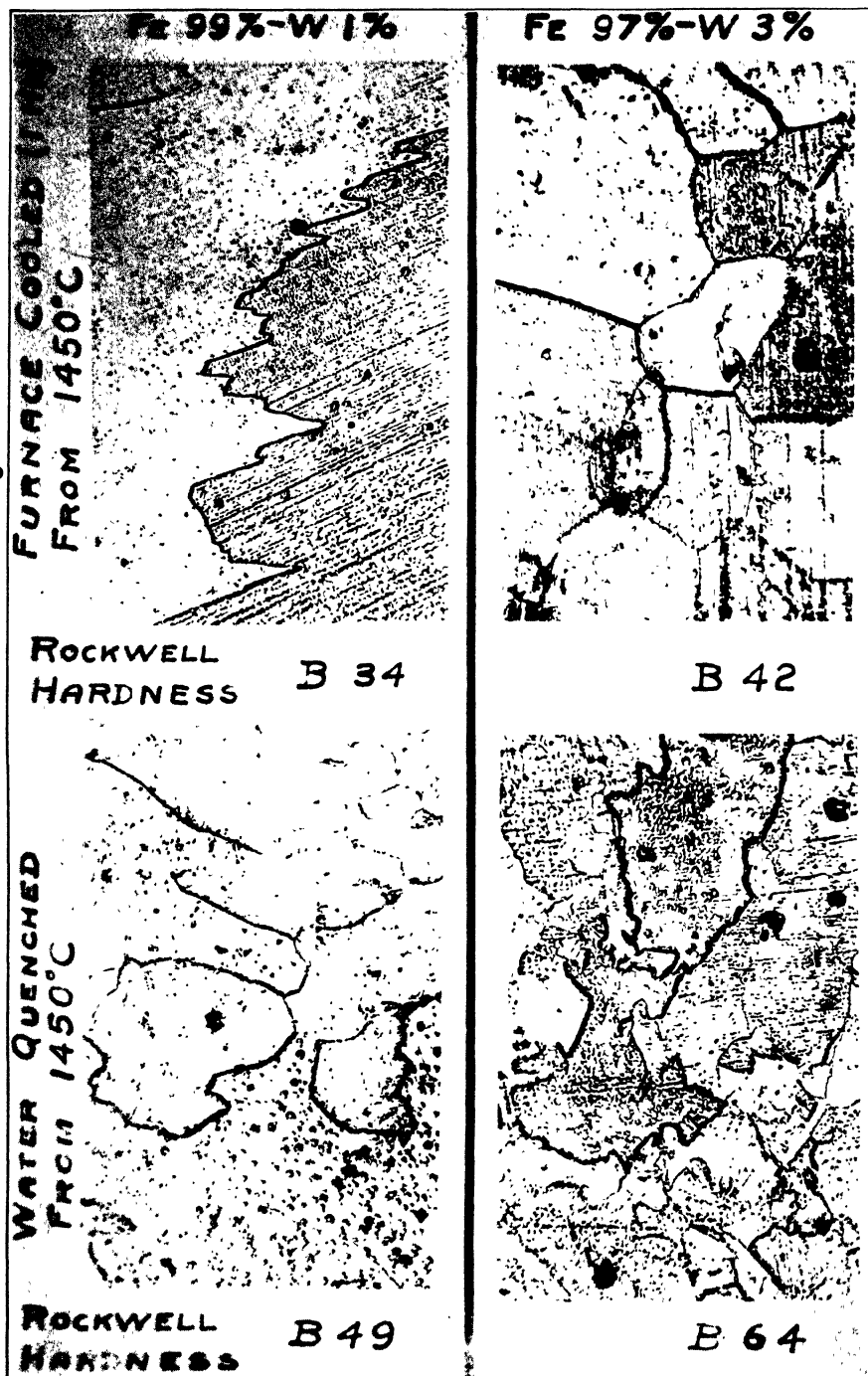
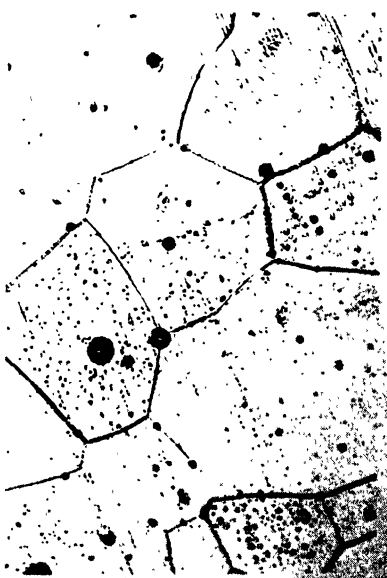


FIG. 26.—EFFECT OF INCREASING TUNGSTEN CONTENT ON THE GRAIN

Fe 95.5%-W 4.5%**B 51****Fe 94%-W 6%****B 60****B 76****B 62**

SIZE OF BOTH WATER-QUENCHED AND FURNACE-COOLED SPECIMENS

The couple was checked with the pure iron specimen several times during the course of the investigation and no change in its characteristics could be detected.

In Fig. 25 are plotted the actual readings, in seconds, of time elapsed between millivolt and temperature intervals for the pure iron and the iron + 4 per cent. tungsten specimens. The positions of the Ar_4 and Ar_3 points for the respective percentages of tungsten are plotted in Fig. 2 along the line MN . The broken portion of the line represents the position of these points and their merging in the range in which they are too weak to be detected.

As has been determined by x-ray analysis, the crystal lattice of pure iron below 900° C. is body-centered cubic; above 900° and presumably up to 1400° its lattice is face-centered cubic.³ Above 1400° C., it again assumes the body-centered lattice⁴ and is designated as delta iron. On the basis of these facts and the shift in the positions of Ar_4 and Ar_3 it would appear that the addition of tungsten to iron tends to prevent the change in lattice from body-centered cubic to face-centered cubic at 1400° C., during cooling from above that temperature.

As the tungsten content increases there is a corresponding decrease in the amount of gamma, or face-centered cubic, iron formed as Ar_4 is passed on cooling. When the tungsten content has reached about 6 per cent., there is apparently but one lattice, the body-centered cubic, present at any temperature.

The grain refinement produced by water quenching from above 1400° C. increases to a marked degree as the tungsten content increases to 5.5 per cent. In the alloys containing 6 per cent. and more of tungsten, the rate of cooling has no perceptible effect upon the grain size.

Fig. 26 illustrates the effect of increasing tungsten content upon the grain size of both water-quenched and furnace-cooled specimens. As the temperature of the Ar_4 transformation is lowered, the conditions become less favorable for the growth of the newly formed grains of gamma iron. By rapid cooling through this temperature range, the opportunity for growth of these grains is still further restricted. At the Ar_3 point, a new set of grains of alpha iron must form from the gamma iron existing above the Ar_3 temperature; a second refinement of grain thus occurs, resulting in the structure shown for the 4.5 per cent. tungsten specimen.

The hardness increase accompanying this grain refinement in alloys containing less than 6 per cent. tungsten in pure iron is shown in Fig. 27. Attention is called to the difference in hardness between pure iron when slowly cooled and when water-quenched from above 1400° C.

³ Arne Westgren: Roentgen Spectrographic Investigations of Iron and Steel. *Jnl. Iron and Steel Inst.* (1921) **103**, 303.

Edgar C. Bain: Studies of Crystal Structure with X-rays. *Chem. & Met. Eng.* (1921) **25**, 657.

⁴ Arne Westgren: *Op. cit.*

To eliminate the grain refinement incident to rapid cooling through the Ar_4 point, four blocks of the 4 per cent. tungsten alloy, after the usual soaking at 1500°C ., were held at 1050°C . for 2 hr. During this time, the gamma iron present will have approached a fairly stable grain size for that temperature. After the 2-hr. heating, two pieces were water-

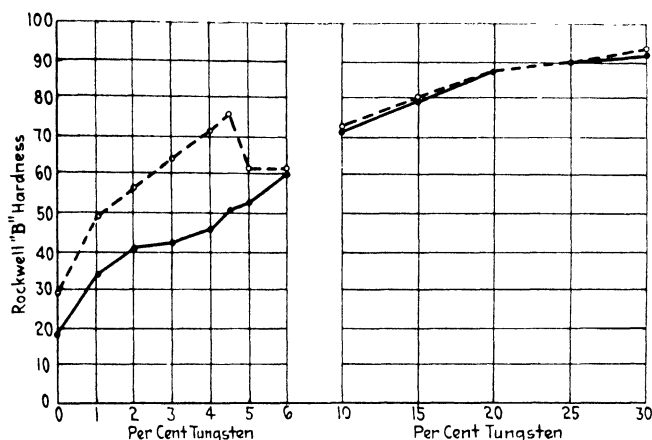


FIG. 27.—ROCKWELL B HARDNESS OF IRON-TUNGSTEN ALLOYS HEATED 2 HR. AT 1500°C . AND WATER-QUENCHED OR FURNACE-COOLED IN 1 HR.

quenched and two cooled in the furnace to about 500°C . in 40 min. The Rockwell hardness numbers of these specimens were as follows:

SPECIMEN	ROCKWELL, AVERAGE OF EIGHT READINGS
Water-quenched 1	B-61
Water-quenched 2	B-60
Furnace-cooled 1	B-48
Furnace-cooled 2	B-49

These figures should be compared with those in Table 2 for the 4 per cent. tungsten alloy as quenched and as slowly cooled from 1500°C . The hardness of the specimens furnace-cooled from 1450°C . is practically the same as that resulting from the slow cooling from 1050°C . However, after quenching from 1500°C ., well above Ar_4 the alloy shows a hardness of B-71, in contrast to the hardness of B-60, when quenched from the 2-hr. heating at 1050°C ., a temperature below Ar_4 but above Ar_3 for that alloy.

As the hardness seems to be determined by the grain size in this series of low-tungsten alloys, the quench through both critical points is considerably more effective in refining the grain than rapid cooling through Ar_3 alone.

TABLE 2.—*Cooling Speed versus Hardness of Iron-Tungsten Alloys; All Specimens Were Heated 2 Hrs. at 1500° C.*

Alloy	Water Quenched				Furnace Cooled 1 Hr. to Black Heat			
	Brinell Hard- ness	Rockwell Hardness			Brinell Hard- ness	Rockwell Hardness		
		Low	High	Average		Low	High	Average
1% W.		B 46	50	B 48		B 30	34	B 33
2% W.		B 58	55	B 56		B 42	39	B 41
3% W.		B 67	62	B 64		B 40	45	B 43
4%.....		B 74	68	B 71		B 45	50	B 47
4.5% W		B 76	74	B 75		B 54	50	B 53
5% W..	112	B 58	62	B 60	108	B 50	58	B 54
6% W. .	118	B 59	62	B 60	112	B 58	64	B 62
10% W.	134	B 72	74	B 73	119	B 71	72	B 71
15% W.	139	B 78	81	B 80	132	B 77	78	B 79
20% W ^a	160	B 87	89	B 88	170	B 87	89	B 88
25% W...	176	B 89	91	B 90	180	B 91	92	B 91
30% W .	182	B 93	94	B 94	184	B 92	94	B 93
Iron.	74	B 26	29	B 28	70	B 15	20	B 18

^a This alloy furnace cooled in 48 hrs. had a Rockwell hardness of B 88.

TABLE 3.—*Hardness of 80 Per Cent. Iron-20 Per Cent. Tungsten, Heated 2 Hr. at 1500° C. and Water-quenched; Heated 1 Hr. at Temperatures from 600° C. to 1400° C.*

Degrees C.	Rockwell Hardness	Brinell Hardness	Degrees C.	Rockwell Hardness	Brinell Hardness
600	B-88	160	1100	B-90	168
700	B-111	315	1200	B-86	162
800	B-112	294	1300	B-88	158
900	B-105	243	1400	B-88	161
1000	B-99	192	Quenched from 1500° C.	B-88	160

HARDNESS MEASUREMENTS

The alloys of the iron-tungsten system exhibit a continuous rise in hardness as the tungsten content is increased up to about 50 per cent. Above that percentage in the tungstide rich range, the alloys tend to become porous and are unsuitable for Brinell or Rockwell measurements. Above 80 per cent. tungsten content, alloys formed below 1650° C. (the decomposition temperature of the tungstide) show a Rockwell hardness of about C 45. This figure drops to C 30 or C 35 for pure tungsten.

The hardness considered thus far is that measured by Rockwell or Brinell standards on alloys as either water quenched from 1500° C. or

furnace-cooled in about 1 hr. from 1500° C. to 500° C. Except the range between 0 and 6 per cent. tungsten, the hardness of a quenched specimen is nearly the same as that of a slowly cooled specimen. In Fig. 28 are plotted the Brinell and Rockwell hardness numbers as measured on a series of iron-tungsten alloys in the quenched condition. Hardness numbers of the alloys as quenched and as slowly cooled are listed in Table 2.

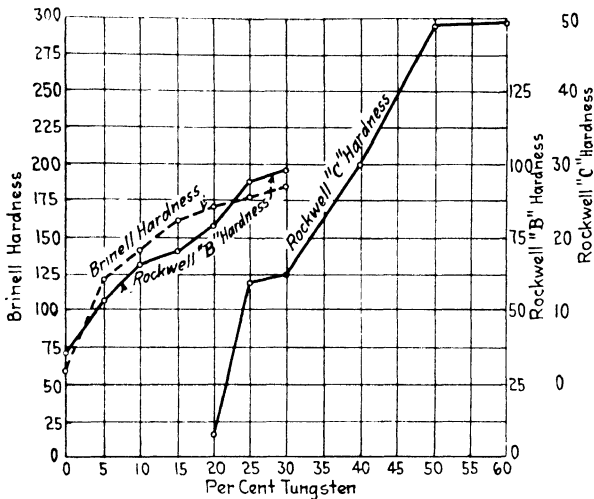


FIG. 28.—IRON-TUNGSTEN ALLOYS WATER-QUENCHED FROM 1500° C.

HARDNESS INCREASE PRODUCED BY AGING

To ascertain what hardening effect, if any, might be produced in the quenched alloys by aging, hardness measurements were taken on a series of blocks of the 20 per cent. tungsten-iron alloy after heating for 1 hr. at temperatures ranging from 600° to 1400° C. The results are recorded in Table 3 and Fig. 29. No increase in hardness was measurable in the specimen aged for 1 hr. at 600° C., but after heating at 700° C. the Brinell hardness had increased by nearly 100 per cent. As the temperature of aging is raised, the resulting hardness becomes less until at 1200° C. it is about that of the alloy in the quenched condition. The 15 per cent. and 25 per cent. tungsten alloys were likewise aged for 1 hr. at the temperatures mentioned and the Brinell measurements obtained are plotted.

Series of specimens from each of six alloys were heated at 700° C. for periods of time ranging from 15 min. to 20 hr. and the corresponding hardness measurements recorded in Tables 4 and 5 and Fig. 30. The increase in hardness resulting from this treatment becomes greater as the tungsten content rises. After aging for 2 hr. at 700° C., the 30 per cent.

tungsten alloy increased in hardness from 196 to 456 Brinell, a gain of about 130 per cent.

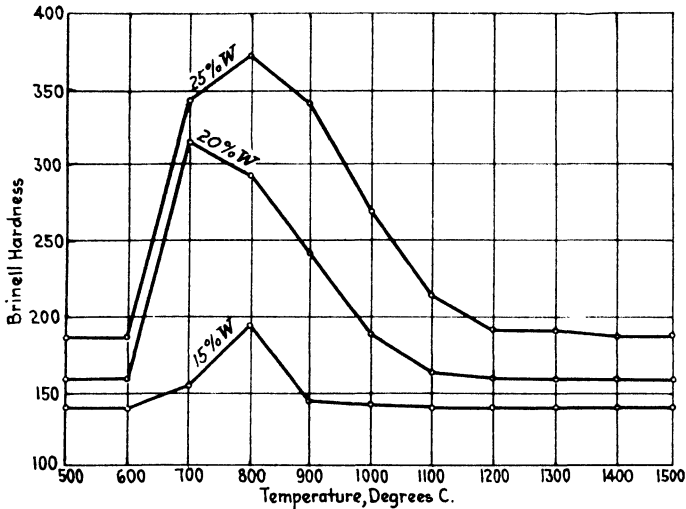


FIG. 29.—BRINELL HARDNESS OF IRON-TUNGSTEN ALLOYS WATER-QUENCHED FROM 1500° C. AND HEATED 1 HR. AT TEMPERATURE INDICATED.

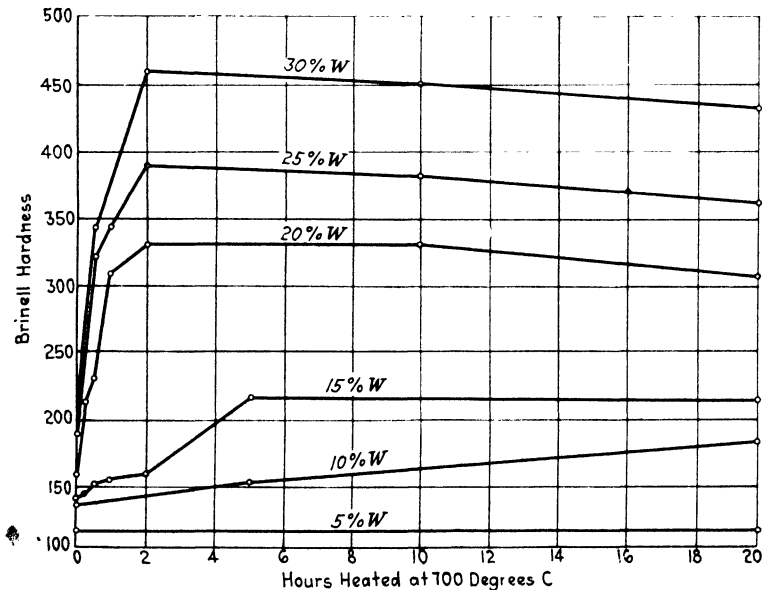


FIG. 30.—INCREASE IN HARDNESS OF IRON-TUNGSTEN ALLOYS WATER-QUENCHED FROM 1500° C. AND HEATED AT ABOUT 700° C.

If the temperature of aging is raised, the hardening will develop more rapidly but the maximum hardness attained will be less than that produced by heating at a lower temperature for a longer time, as shown by

the curves in Figs. 31 and 32. After heating for 1 hr. at 800° C. the 15 per cent. alloy has a Brinell hardness of 194, while the hardness measure-

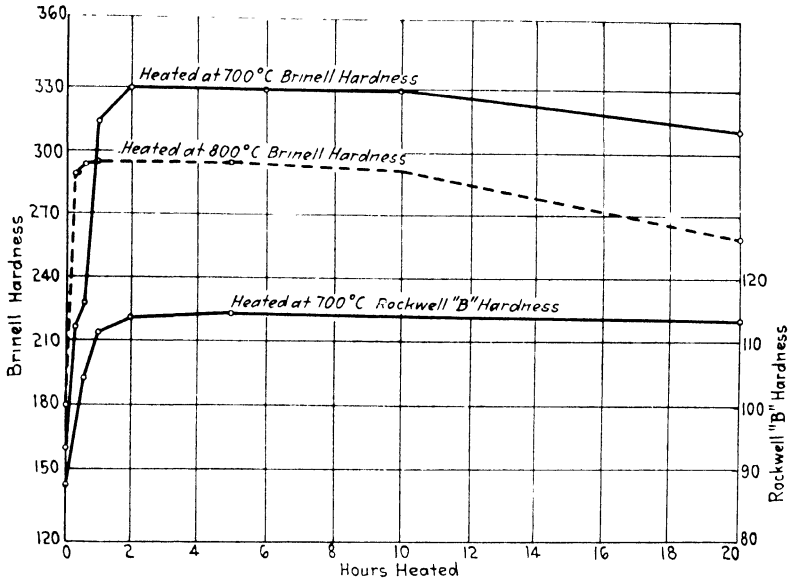


FIG. 31.—INCREASE IN HARDNESS OF 20 PER CENT. TUNGSTEN, 80 PER CENT. IRON ALLOY, WATER-QUENCHED FROM 1500° C.

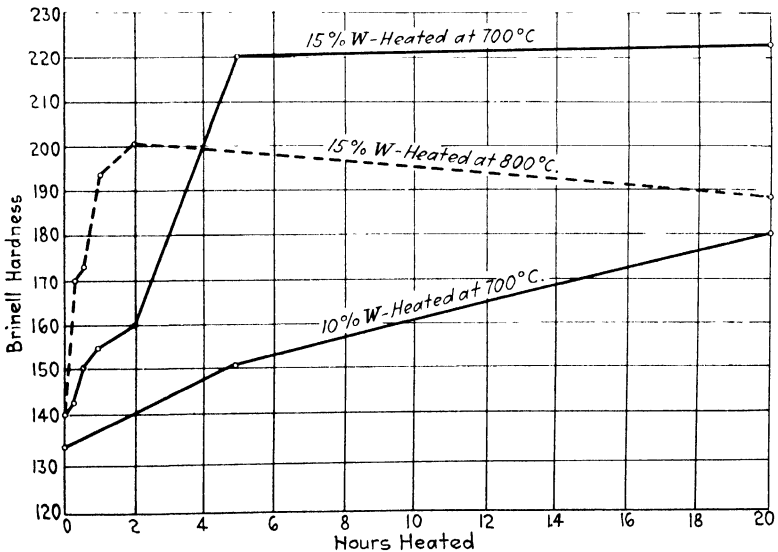


FIG. 32.—INCREASE IN HARDNESS OF IRON-TUNGSTEN ALLOYS WATER-QUENCHED FROM 1500° C.

ment on the specimen heated at 700° C. for the same period is but 155. However, after 20 hr. at 700° C. the Brinell hardness measures 223, while

the maximum hardness produced by aging at 800° C. is 201 after 2 hr. and after 20 hr. the hardness measures but 188.

The same effect is shown in the 20 per cent. tungsten alloy, for which are plotted in Fig. 31 the hardness measurements after aging at 700° C. and 800° C. When aged at 600° C. for 300 hr. the 20 per cent. tungsten alloy develops a Brinell hardness of 340—slightly higher than the maximum attained by aging at 700° C., further heating results in a decrease in hardness. The 15 per cent. tungsten alloy, after 440 hr. at 600° C., shows a Brinell hardness about equal to the highest developed during the 700° C. aging of this material; see Fig. 33 and Table 4.

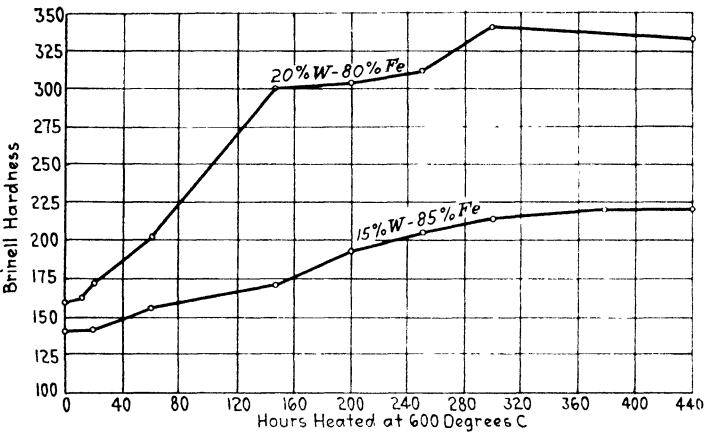


FIG. 33.—INCREASE IN HARDNESS OF IRON-TUNGSTEN ALLOYS WATER-QUENCHED FROM 1500° C.; AGED AT 600° C.

TABLE 4.—*Brinell Hardness of Iron-tungsten Alloys Water-quenched from 1500° C. and Aged at 700° and 800° C.*

Alloy	As Quenched	Held at 700°, Hours							Held at 800°, Hours						
		¼	½	1	2	5	16	20	¼	½	1	2	5	10	20
Iron + 5 % W ..	111					108		111							
+10 % W	134			130		151		180							
+15 % W ..	139	144	151	155	160	220		223	170	173	194	201			188
+20 % W	160	213	228	315	330		330	312	290	293	294		294	292	260
+25 % W.....	184		320	346	391	391	385	360	356	372	372	356	332		312
+30 % W....	196		344	420	456		450	430							

The changes in microstructure accompanying the increase in hardness with aging are illustrated in Figs. 34 to 39. These photomicrographs represent steps in the aging of an alloy of 80 per cent. iron 20 per cent. tungsten, the structure of which, as quenched, is shown in Fig. 2. In the quenched condition its Brinell hardness is 160. After aging 2 hr. at 700° C. the Brinell hardness has increased to 330. A polished section

TABLE 5.—*Rockwell Hardness of Iron-tungsten Alloys Water-quenched from 1500° C. and Aged at 700° and 800° C.*

Alloy	As Quenched	Held at 700°, Hours					Held at 800°, Hours								
		¼	½	1	2	3	5	20	¼	½	1	2	3	5	20
Iron +15% W.	B 80			B 90	B 99	B 100	B 101	B 98			B 94	B 97	B 97	B 95	B 93
+20% W. . .	B 88		B 104	B 111	B 113		B 114	B 113			C 13	C 14	C 16	C 12	C 11
	B 94									B 111	B 112	B 112		B 110	
+30% W.	C 15	C 30	C 45	C 47	C 49		C 52	C 48							
+40% W.	C 30			C 53		C 54		C 55							
+50% W.	C 48						C 52	C 53							
+60% W.	C 49						C 50								



FIG. 34.—TUNGSTEN 20 PER CENT., IRON 80 PER CENT.; QUENCHED FROM 1500° C AND AGED 2 HR. AT 700° C., BRINELL HARDNESS 330. $\times 1000$.



FIG. 35.—TUNGSTEN 20 PER CENT., IRON 80 PER CENT.; QUENCHED FROM 1500° C. AND AGED 20 HR. AT 700° C.; BRINELL HARDNESS 312. $\times 1000$.

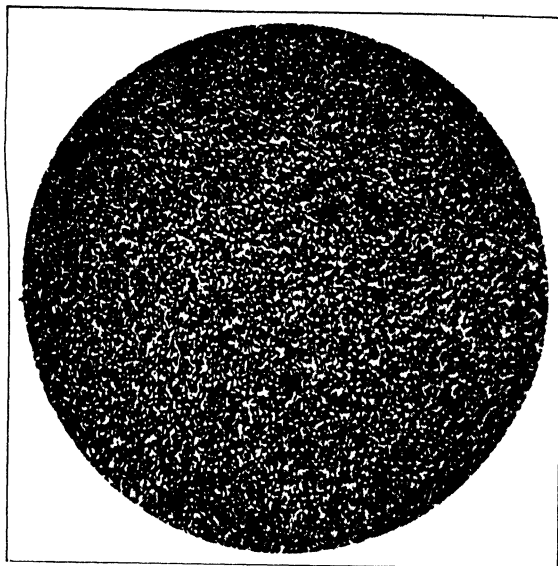


FIG. 36.—TUNGSTEN 20 PER CENT., IRON 80 PER CENT.; QUENCHED FROM 1500°C AND AGED 20 HR. AT 800°C .; BRINELL HARDNESS 260. $\times 500$.

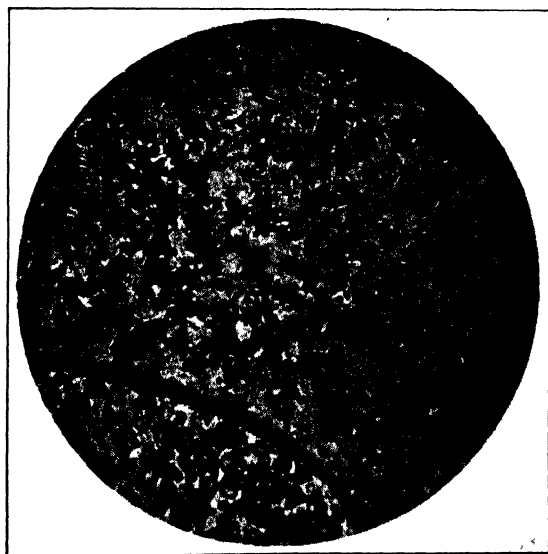


FIG. 37.—TUNGSTEN 20 PER CENT., IRON 80 PER CENT.; QUENCHED FROM 1500°C . AND AGED 20 HR. AT 800°C .; BRINELL HARDNESS 260. $\times 1000$.

after this aging darkens quickly in the etching reagent, 10 per cent. nitric acid in alcohol. The etching characteristics of the aged alloys resemble those of a quenched and tempered steel. Fig 34 shows the etch-darkened

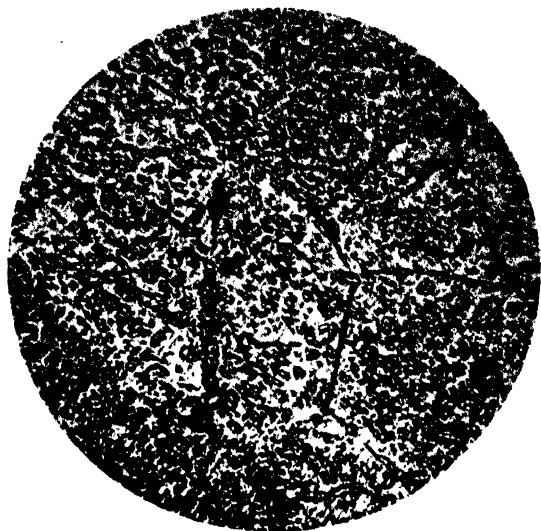


FIG. 38.—TUNGSTEN 20 PER CENT., IRON 80 PER CENT.; QUENCHED FROM 1500° C. AND AGED 1 HR. AT 1000° C. AND QUENCHED; BRINELL HARDNESS 180. $\times 500$.

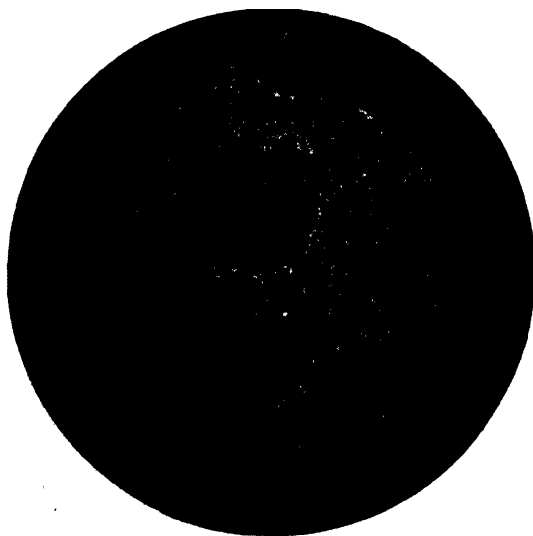


FIG. 39.—TUNGSTEN 20 PER CENT., IRON 80 PER CENT.; QUENCHED FROM 1500° C. AND AGED 1 HR. AT 1200° C. AND QUENCHED; BRINELL HARDNESS 160. $\times 500$.

surface of the alloy aged to develop its maximum hardness; a slight precipitate of unetched tungstite is visible at the grain boundaries.

After 20 hours at 700° C. the Brinell hardness has dropped to 312; Fig. 35 shows a section of this specimen. The grain boundary precipitate seems to have increased slightly in volume. Throughout the darkened ground mass, however, no individual particles can be resolved at 2000 magnifications. After aging this alloy for 20 hr. at 800° C., the precipitated tungstide can readily be seen scattered through the grains as well as at the grain boundaries; Figs. 36 and 37 illustrate this structure. The Brinell hardness of 260 at this stage of aging is 75 per cent. above that of the quenched alloy but only about 80 per cent. of the maximum hardness developed by aging at 700° C. By aging at still higher temperatures, the particle size of the precipitate is increased and the corresponding Brinell hardness lowered; see Figs. 38 and 39.

VOLUME CHANGE DURING AGING

Cubes measuring about 0.5 in. on the edge were prepared from alloys containing 10, 20 and 30 per cent. tungsten. These cubes were quenched

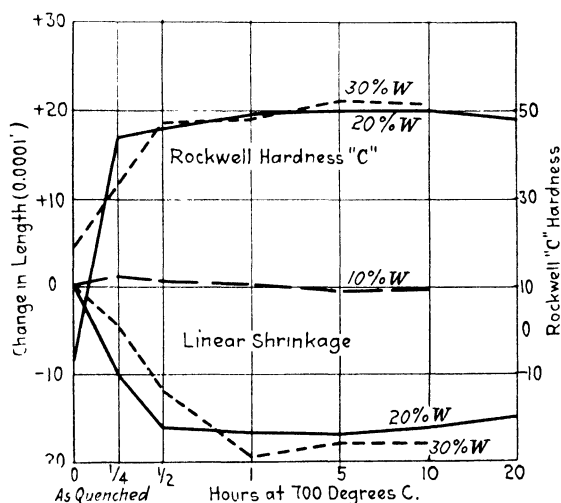


FIG. 40.—CHANGE IN DIMENSION AND HARDNESS OF IRON-TUNGSTEN ALLOYS QUENCHED FROM 1500° C. AND AGED AT 700° C.

from 1500° C., two opposite faces on each ground and measurements made to 0.0001 in. between the ground faces. They were aged in an electric furnace and hydrogen atmosphere at 700° C. \pm 10° C. for periods of time varying from 15 min. to 10 hr. By cooling the blocks in a water-cooled hydrogen chamber attached to the rear of the furnace, surface oxidation was completely prevented.

Measurements made on the blocks after aging showed a shrinkage in the case of the 20 per cent. and 30 per cent. tungsten alloys. This shrinkage increases with the aging time and appears to reach a maximum

in these specimens in which the hardness has reached its high value. In the case of the 30 per cent. alloy aged for 1 hr. at 700° C., the dimension has decreased 0.0020 in. in 0.522 in. or about 0.4 per cent. The changes in dimension and hardness with increased aging time are plotted in Fig. 40.

CHANGE IN PHYSICAL PROPERTIES OF 15 PER CENT. TUNGSTEN-IRON ALLOY PRODUCED BY AGING

Several rods of the 15 per cent. tungsten alloy 0.350 in. square were reduced in cross-section by about 80 per cent. by swaging at a temperature of 700° to 800° C. Test bars 5 in. long were turned from these rods to a diameter of 0.150 in. over a length of 3 in. In Table 6 and Fig. 41

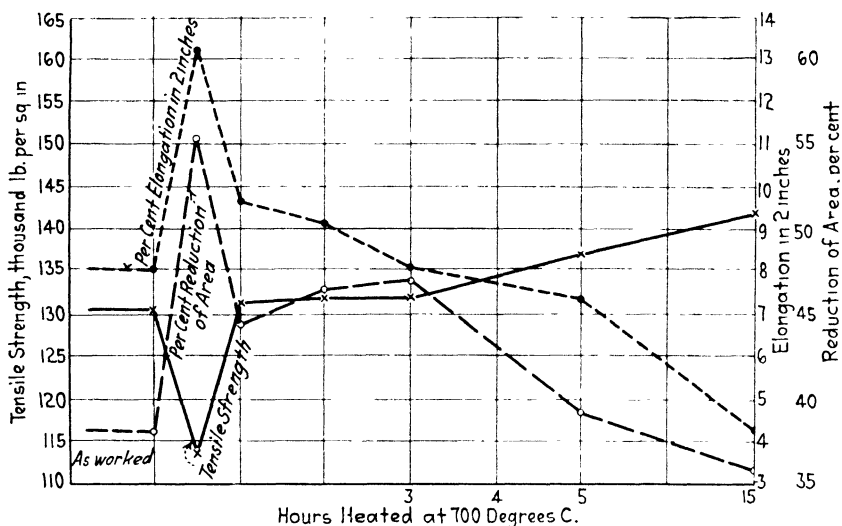


FIG. 41.—CHANGES IN PHYSICAL PROPERTIES OF 15 PER CENT. TUNGSTEN, 85 PER CENT. IRON ALLOY REDUCED 80 PER CENT. BY SWAGING AT 700°-800° C. AND AGED AT 700° C.

are recorded the results of tensile tests on these rods as worked and after aging at 700° C. for periods of time ranging from $\frac{1}{2}$ to 15 hr.

Heating at 700° C. for $\frac{1}{2}$ hr. results in a fall in tensile strength and increase in both elongation and reduction of area; this may reasonably be ascribed to the annealing that would take place in iron at this temperature. After another $\frac{1}{2}$ hr. at 700° C., the tensile strength rises slightly above that of the unaged alloy and continues to increase until, after 15 hr. heating, it has reached 142,000 lb. per sq. in., representing an increase of about 9 per cent. The elongation and reduction in area have suffered a corresponding decrease. As the material was worked at temperatures between 700° and 800° C. it seemed probably that a considerable aging effect had occurred during swaging. In that case the

tensile properties of the swaged material would be the result first of, the hardening due to working and, second, of the hardening due to a certain amount of aging at the working temperatures.

TABLE 6.—*Physical Properties of 15 Per Cent. Tungsten-85 Per Cent. Iron Alloy Reduced 80 Per Cent. in Area by Swaging at 700–800° C. Diameter of Test Piece 0.150 In.*

Treatment	Tensile Strength, lb per Sq In.	Per Cent. Elongation in 2 In.	Per Cent. Reduction of Area
As swaged	130,500	8 00	38.0
Heated 700° C. $\frac{1}{2}$ hr	114,000	13 25	55.5
1 hr.	131,500	9 75	44.5
2 hr.	132,000	9 10	46.5
3 hr	132,000	8 10	47 0
5 hr	136,700	7 40	39 0
15 hr	142,400	4 10	36 0
Heated 1450° C. $\frac{1}{2}$ hr. and quenched in water	54,500	3 2	8 0

Averages of three tests in each instance.

To eliminate both of these factors, several of the test rods were heated to 1450° C. for 1 hr. and water-quenched. The results of the tensile

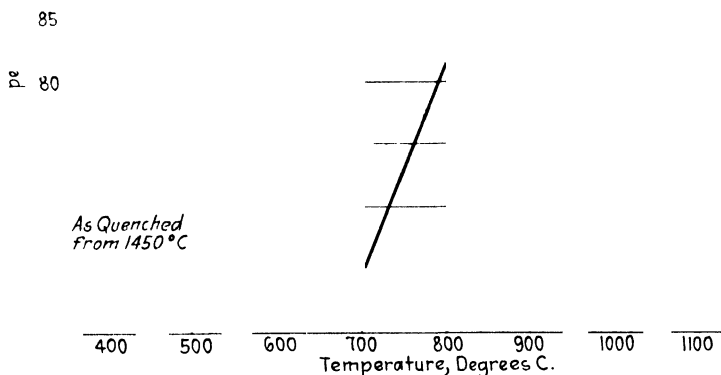


FIG. 42.—TENSILE STRENGTH OF 15 PER CENT. TUNGSTEN, 85 PER CENT. IRON ALLOY REDUCED 80 PER CENT. BY SWAGING, HEATED $\frac{1}{2}$ HR. AT 1450° C. AND WATER-QUENCHED, THEN HEATED 1 HR. AT DIFFERENT TEMPERATURES.

tests on these rods are recorded in the bottom line in Table 6. Note the very much lower tensile strength, elongation, and reduction. Heating at 1450° C. develops a very coarse grain in this alloy, which results in erratic elongation and reduction of area in the tensile test. The tensile strengths of individual test rods, however, check fairly closely.

A number of test rods quenched from 1450° C., were heated for 1 hr. at temperatures ranging from 500° to 1200° C.; Fig. 42 shows the resulting

tensile strength. The sudden jump in strength after heating at 800° C. is apparently due to the same action that brings about the increase in hardness in this range of temperature. Also, the rise in strength in the quenched alloy amounts to more than 25 per cent. against the 9 per cent. increase produced by aging the alloy in the worked condition. This contrast indicates that undoubtedly a part of the aging action had taken place during the swaging operations and hence was not available to increase the tensile strength on subsequent aging at 700° C.

GENERAL DISCUSSION

A notably similar example of hardening by aging is found in the aluminum-copper alloy system. Aluminum alloys of the duralumin type, when quenched from 500° C., increase in hardness about 50 per cent. by subsequent aging. Merica, Waltenberg, and Scott,⁵ after a study of these alloys, attributed this hardening to the compound CuAl_2 , which is precipitated in a finely divided state during the aging process. When aged at temperatures of 150° to 200° C., the hardness of these alloys first increases to a maximum and then decreases. "During that aging, there has been a formation of fine nuclei of CuAl_2 followed by coalescence of these particles into ones of large size." These authors deduce from the results of their study that "there is a certain average size of particle of CuAl_2 for which the hardness of the material is a maximum."

If in the conclusions just quoted we substitute Fe_3W_2 for CuAl_2 the conclusions are fully as applicable to the observed performance of iron-tungsten alloys upon aging.

The theory of the type of hardening illustrated in these two alloy systems has been further developed and formulated by Jeffries and Archer.⁶

A preliminary exploration of the iron-molybdenum system reveals striking similarities between it and the iron-tungsten system. Equal atomic percentages of molybdenum and tungsten displace the Ar_4 and Ar_3 points in iron to practically the same degree.

There appears to be a eutectic at about 35 per cent. by weight of molybdenum, melting a temperature close to 1450° C. A compound is formed at the composition 53 per cent. molybdenum 47 per cent. iron, corresponding to the formula Fe_3Mo_2 . The solid solution of 22 per cent. molybdenum in iron, quenched from 1400° C. will develop, after aging at 600° C., a Brinell hardness greater than 500.

Alloys of the iron-tungsten and the iron-molybdenum systems, as hardened by aging, have been recently used in place of high-speed steel

⁵ P. D. Merica, R. G. Waltenberg, and H. Scott: Heat Treatment and Constitution of Duralumin. *Trans.* (1920) **64**, 41.

⁶ Zay Jeffries and R. S. Archer: The Slip Interference Theory of the Hardening of Metals. *Chem. & Met. Eng.* (June 5, 1921); also "The Science of Metals," 411.

for certain purposes at the Cleveland Wire Division. The results have been most satisfactory in that the useful life of these alloys is from ten to forty times that of high-speed steel.

ACKNOWLEDGMENTS

Some of the material pertaining to the hardness and tensile properties of the iron-tungsten alloys is taken from the work of J. H. McDaniel, G. M. Hale, and J. K. Johnson, which was done at the Cleveland Wire Division, under the guidance of the author, in 1924 and submitted by them as theses to Case School of Applied Science for their B. S. degrees in Metallurgical Engineering.

The cooling curves taken in determining the positions of the critical points in the low-tungsten alloys were obtained with the assistance of P. P. Tarasov, metallurgist at the Cleveland Wire Division, by whose aid this phase of the work was completed.

The precision measurements on the blocks of the alloys, as quenched and aged, were obtained with the generous coöperation of T. L. Robinson of the Marlin Rockwell Corp., Chicago, Ill. I wish to thank Dr. Zay Jeffries for many inspiring suggestions also A. B. Gladding for helpful ideas in connection with this investigation.

SUMMARY

The system iron-tungsten comprises: (a) solid solution of tungsten in iron, 33 per cent. of tungsten being soluble at 1525° C. and 8 per cent. at room temperature. (b) A eutectic at 49 per cent. tungsten, being a conglomerate of the compound Fe_3W_2 and the solid solution of tungsten in iron. (c) The compound iron tungstide (Fe_3W_2) at the composition 68.7 per cent. tungsten. (d) Beyond this composition there may be present, if below 1650° C., the compound + iron in tungsten solid solution. If heated above 1650° C., the iron tungstide partly decomposes into iron-rich and tungsten-rich phases. (e) Tungsten dissolving 1.2 per cent. iron at 1600° C.

The critical point Ar_4 is lowered from 1400° to 1200° C. and the point Ar_3 is raised from 890° to 980° C. by the addition of 5.5 per cent. tungsten to iron.

The Brinell and Rockwell hardness of iron increases continuously with the addition of tungsten in amounts up to about 50 per cent. by weight.

The hardness of some of these alloys, water-quenched from 1500° C., is increased as much as 130 per cent. by aging at temperatures from 600° to 700° C.

In aging at a given temperature, the hardness reaches a maximum and then decreases as aging is prolonged.

The higher the temperature of aging, above a certain minimum temperature, the more rapidly the hardness increases, but the lower is the maximum hardness attained.

The tensile strength is affected by aging in the same manner as the hardness; a decrease in ductility accompanies the increase in tensile strength.

Development of secondary hardness in these alloys is accompanied by precipitation of the compound Fe_3W_2 . The particle size of the precipitate remains submicroscopic until the hardness has passed through its maximum value and has fallen off considerably.

A shrinkage in volume takes place during the aging process and, in general, its maximum is coincident with that of the hardness produced by aging.

DISCUSSION

W. P. SYKES (written discussion).—Some recent work preliminary to a thorough study of the iron-tungsten-carbon series indicates the effect

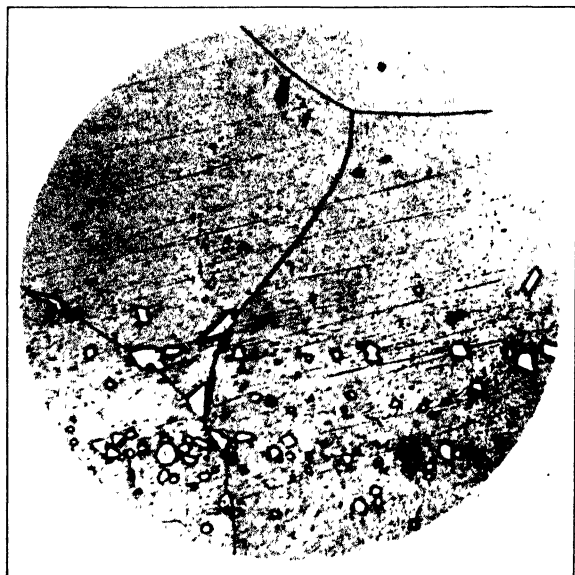


FIG. 43.—COARSE-GRAINED, SOLID SOLUTION OF TUNGSTEN IN DELTA IRON NEAR SURFACE OF DECARBURIZED HIGH-SPEED STEEL. WATER-QUENCHED FROM 1300°C . $\times 500$.

of carbon on certain properties of the iron-rich iron tungsten alloys. With a fixed tungsten content the addition of carbon increases the hardness of the alloy as quenched from 1200 to 1300°C ., but at the same time lowers the secondary hardness produced by subsequent aging at a lower temperature.

The following experiment illustrates in part the above mentioned effect. A block of high speed steel (tungsten 17 to 18 per cent.; carbon 0.50 to 0.60 per cent.) was heated in hydrogen at 1300° C. for 3 hr. and quenched in water. A section of this block, $\frac{3}{16}$ in. below the surface,

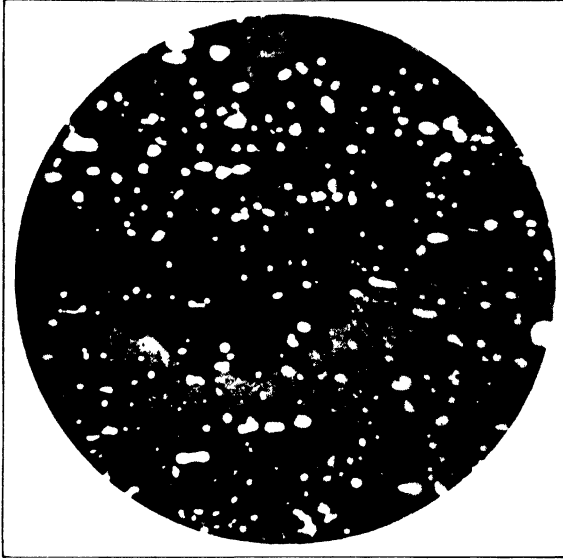


FIG. 44 —BOUNDARY LINE BETWEEN NORMAL CENTER (LIGHT) AND PARTIALLY DECARBURIZED OUTER SURFACE (DARK). WATER-QUENCHED FROM 1300° C. $\times 500$.

after polishing and etching, showed an outer shell about $\frac{1}{8}$ in. deep of more or less completely decarburized metal. Near the surface the structure is that of the coarse-grained solid solution of tungsten in delta iron. (Fig. 43.) This is a characteristic of the carbon-free iron tungsten alloys containing that percentage of tungsten present in this steel.

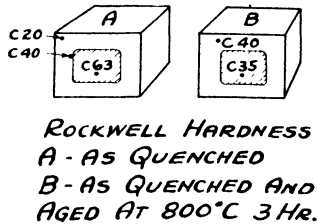


FIG. 45.- -ROCKWELL HARDNESS NUMBERS OF HIGH-SPEED STEEL HEATED 3 HR. IN HYDROGEN AT 1300° C. AND QUENCHED IN WATER.

Nearer the center the grains become smaller and the carbide particles more numerous, suggesting a gradual increase in carbon content from the outer portions toward the center. About $\frac{1}{8}$ in. from the surface appears a very sharply defined boundary line between the partially decarburized exterior and the center of normal high-speed steel structure.

In the micrograph (Fig. 44) the darker portion is nearer the surface. Decarburization has proceeded from this direction toward the center or lighter area. It is of interest to note that the contour of the boundary seems to be largely determined by the positions of the unetched particles, the so-called complex carbides of the high-speed steel.

In Fig. 45 are indicated the Rockwell hardness numbers in the outer and inner portions of this block, both as quenched and after subsequent aging at 800° C. Note that the outer decarburized portion behaves upon aging as the pure iron tungsten alloy. The center, on the other hand, has fallen off decidedly from its quenched hardness of C-63, until it is now softer than the low-carbon or carbon-free exterior.

Z. JEFFRIES, Cleveland, O. (written discussion).—This work of Sykes I believe constitutes the beginning of a new art which will include the hardening of carbonless-iron alloys and the heat treatment of iron alloys in which gamma iron plays no rôle. Already this work has resulted in the production of an alloy, which has superior red hardness to high speed steel.

The paper reflects the careful work of the author in the determination of the solidus and liquidus lines but, what is more important, the changes in the solid state have been carefully determined and incorporated in the diagram. There are a number of points in this paper which could be discussed with profit, but I should like, to point out in particular the relation of some of Sykes' work to the quantitative estimation of some of the factors which increase hardness by slip-interference.

For convenience I shall refer to some of the results of Sykes on the carbon-free iron molybdenum alloys described by me Dec. 3, 1925, in the First Robert Henry Thurston Lecture at the annual meeting of the American Society of Mechanical Engineers. A carbon-free alloy containing 78 per cent. of iron and 22 per cent. of molybdenum by weight when quenched from a high temperature, was found to be a solid solution with a hardness of 214 Brinell. On heating to from 600 to 650° C. for an extended period, the hardness was increased to about 530 Brinell. One great value in the study of these alloys from the theoretical standpoint is that there is no allotropic change in the iron. We can thus follow the hardness changes due to certain structural changes without the complication of an allotropic change on any change in grain size.

The Brinell hardness of the nearly pure coarse-grained iron with which Sykes worked, is in the neighborhood of 70. It has been found that the increased hardness due to molybdenum in solid solution, is nearly proportional to the atoms per cent. of molybdenum. This is true whether the iron is undersaturated or supersaturated. Mr. Archer has made similar observations on the effect of copper in solid solution in aluminum. The increase in hardness of iron produced by adding 14 atoms per cent. of molybdenum in solid solution was in one instance between 140 and 150

points Brinell. The further increase in hardness of this solid solution produced by causing the association of some of the molybdenum with some of the iron to form many highly-dispersed particles of compound, was in one instance about 315 points Brinell. However, to provide the atoms to form a compound the iron molybdenum solid solution becomes less concentrated in molybdenum. In the hardened alloy it seems that the solid solution contains not more than six atoms per cent. of molybdenum. The hardness of the iron molybdenum alloy containing about 6 atoms per cent. molybdenum, is 130 Brinell. In the final hardened alloy with a Brinell hardness number of 530, the iron without change in grain size or without allotropic modification has been increased in hardness from 70 to 530. Of this increase of 460 points Brinell, about 60 points are attributed to the molybdenum in solid solution and 400 points to the high dispersion of hard particles of the iron molybdenum compound.

Similar quantitative estimates on aluminum alloys have been made by Archer and myself with results of the same order of magnitude as to the part played by solid solutions and by the presence of highly-dispersed particles of compound. Mr. Dean and his associates have provided the basis for such calculations in the lead-antimony alloys and it can readily be calculated from their results that the lead-antimony alloys in their hardest condition owe their high hardness chiefly to finely-dispersed particles of antimony rather than to the solid solution of antimony in lead.

Archer and I had these considerations with respect to aluminum before us when we attributed the chief cause of the hardness of freshly-hardened steel to grain refinement rather than to a solid solution of carbon in iron. The evidence is overwhelming that in freshly-formed martensite most of the carbon is atomically dispersed and the fact is clear that such material is very hard. The precipitation of the carbide in highly-dispersed particles should ordinarily produce a marked increase in hardness, but in martensite the increase is only slight. This fact leads to the conclusion that slip resistance factors are present before the carbide precipitation, sufficient to develop nearly the maximum cohesion of the iron. The evidence was fairly strong a few years ago and is still stronger today that this hardness of freshly-formed martensite is not due chiefly to the fact that the carbon is in solid solution in the iron. One way of developing high resistance to slip, is by grain refinement or the great refinement of the general structure of an alloy. The evidence is overwhelming that the grain size of the body-centered crystals of iron in martensite is extremely small. The final conclusion is that the great hardness of freshly-formed martensite is due primarily to grain refinement.

The additional evidence that a coarse-grained solid solution of carbon in body-centered crystals of iron cannot account for the hardness of martensite, is provided by Bain who has preserved solid solutions of carbon in coarse-grained crystals of body-centered cubic iron-chromium alloys and by Sykes who has done the same in the iron-tungsten and iron-

molybdenum alloys. The latter solid solutions are hardened by the carbon only to an extent comparable with the effect of carbon on gamma iron which is not nearly sufficient to account for the high hardness of freshly-formed martensite.

It is therefore apparent that these researches aside from other value, throw much light on the whole problem of the hardening and hardness of steel.

M. A. GROSSMANN, Canton, O.—It seems fitting to discuss the two previous papers together as they both bring out the existence of the gamma iron loop; that is, the fact that beyond a certain percentage of alloying element there is no transformation to gamma iron, there being merely alpha or alpha continuous to delta. This seemed to offer a possible explanation for certain phenomena that have been observed in alloy steels or in ferrous alloys other than those described by Mr. Sykes and Mr. Bain.

It is especially interesting because we find here a confirmation of a theory put forward about 10 years ago by Tammann that such a condition was possible, and it has now been proved by Mr. Sykes for iron and tungsten, and by Mr. Bain for iron and chromium, and within the past 6 to 18 months for iron and silicon by Oberhoffer; also reviewed by Wever for Oberhoffer's iron-silicon diagram and shown by him for iron and tin; and more recently by Maurer for iron and vanadium.

It is in connection with the iron-silicon alloys and also the iron-vanadium alloys that certain evidence has come forward that is of practical interest. About 3 or 4 years ago we encountered some unexplained phenomena in high-speed steel which contained approximately $3\frac{1}{2}$ to 4 per cent. vanadium, the unexplained phenomena being a peculiar softness at all working temperatures—1600 to 2300° F.—and also a complete inability to harden these alloys by any quenching treatment beginning at 1500 or 1600° and up to the customary high-speed steel hardening temperatures at 2300 to 2400°. This would be explained by Maurer's evidence on the iron-vanadium diagram. In connection with the iron-silicon alloys the phenomenon is somewhat better known and explains the reason why transformer iron containing 4 per cent. silicon and almost no carbon can be annealed at almost any desired temperature so as to increase the grain size without encountering any transformations to gamma iron which because of recrystallization would tend to decrease the grain size.

MEMBER.—I recently took 20 per cent. chromium and 1 per cent. carbon in connection with hardening. I found that the hardness increases up to 1900° F., with a very sharp dropping off above that, the Rockwell reading on a piece hardened at 2200° being only 42. The pieces hardened above 1900° do not increase in hardness but decrease if anything, whereas the pieces in the range from 1800 to 2000° increase on tempering temperatures running up to about 800° F.

Probable Error in Blast-furnace Records and Calculations Therefrom

By T. T. READ,* WASHINGTON, D. C.

(New York Meeting, February, 1925)

A SHORT time ago, one of the large steel companies courteously furnished the author with detailed records of the operations of a considerable number of iron blast furnaces over a period of two months. These will be made the basis of a subsequent study, but in beginning this study one of the first points requiring consideration was the probable error of the records, for what otherwise might be regarded as significant differences of performance under different conditions were perhaps really due to errors of observation, or failure to observe and record variations.

If it is assumed, in blast-furnace records and calculations, that known quantities or factors are constant, when as a matter of fact they are variable, the effects of these variations may erroneously be ascribed to some other cause. This is quite clearly expressed in the following quotation from E. Buckingham:¹

Theory always operates on an ideally simplified picture of reality because real phenomena are unmanageably complicated. The results obtained are not exactly true for any real phenomenon, though they may be for an ideal one; and the approximation with which a theoretical equation, however obtained, represents the actual facts, always depends on the approximation in essentials between the ideal picture and its real prototype.

The purpose of dimensional reasoning is to find out how some quantity which is involved in the phenomenon under consideration is related to certain others; or to find the relation connecting two or more quantities which vary, or may vary, simultaneously during the course of the phenomenon. Since we know that we must have a complete equation to start with, we begin by thinking the matter over, to see whether the quantities we have in mind are the only ones involved. Usually it is evident that they are not; so we next make a list of all the quantities we can think of which might under any circumstances be important. Upon considering this list, which is often a long one, it is usually evident that under the actual circumstances a number of these quantities may safely be ignored; so we cross them off the list and thus pass from our most general conception of the phenomenon to an ideal simpler one, in which these quantities are not involved at all.

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¹ Notes on the Method of Dimensions, *Phil. Mag.* (1921) 42, 698.

The decision as to whether, under the given circumstances, a quantity may safely be ignored introduces the possibility of error. This can best be illustrated by specific examples taken from blast-furnace practice. The chemical substances involved in blast-furnace operation are, in the order of relative weights involved, nitrogen, oxygen, iron, carbon, silicon, aluminum, calcium, magnesium, and a long list of others that are usually ignored, except sulfur and phosphorus, which produce marked effects even though present in only small amounts.

The only way in which the nitrogen enters the furnace in appreciable amounts is in the blast. Its principal effect is to cool down the zone of combustion, as in modern practice the temperature of the top gases is roughly only one-third that of the blast. Therefore, the principal effect of the nitrogen on the blast-furnace process is simply the transferring of heat from the combustion zone to higher levels in the shaft. Errors in the measurement of the large quantities of nitrogen involved are, therefore, less important than they are in the case of the other chemical substances.

This is not true of the oxygen, which principally enters with the blast (both as free oxygen and in the form of water vapor), although it also enters combined with iron, silicon, aluminum, etc. The total amount of oxygen can be reckoned in pounds and the combined oxygen offers no special difficulty if the weights and the analysis of each of the combinations are known. The oxygen of the blast is much more difficult to reckon accurately, and the method will be discussed in some detail. To save repetition, it may be stated here that the constants used have been taken from the Smithsonian Physical Tables, 7th revised edition.

The amount of blast entering a blast furnace can easiest be recorded in cubic feet; an ordinary blast furnace in the Pittsburgh district uses about 40,000 cu. ft. per min. A revolution-counter on the blowing engine and a determination of the number of cubic feet blown per revolution would enable this measurement to be made quite accurately if it were only possible to make an accurate determination of the number of cubic feet of free air blown per revolution of the blowing engines. For that, it would be necessary to know accurately the true volumetric efficiency of the blowing engines, and this undoubtedly varies with variation in the ratio of the intake pressure to the delivered pressure, the speed of the engines, the condition of the piston rings, piston-rod packing, valves, and other factors. Even then, the air is not in the furnace; leaks in valves, pipe connections, stoves, and furnace connections must be taken into account. Most blowing engines bear, on their sides, a plate that states that they deliver so many cubic feet of free air per minute when running at a specified number of revolutions per minute. What the probable accuracy of the initial measurement is I do not know, nor do there seem to be available any determinations of the magnitude of the

variables just mentioned. If we simply cross them off as capable of being ignored, we must not at the same time ignore the fact that the probable error in the measurement of the air has been greatly increased by leaving them out of consideration. We can only guess the probable error thus introduced, but a combination of all the sources of error probably would amount to a plus or minus error of 10 per cent. in the cubic feet of air recorded as blown per minute, usually on the positive side.

But even if we could determine the number of cubic feet of free air accurately, we would not be out of difficulty because cubic feet are of no use to us, what we need to know is the number of pounds of oxygen, and unfortunately the number of pounds of oxygen in 1000 cu. ft. of free air is quite variable. The weight of 1000 cu. ft. of dry air at 32° F., 760 mm. pressure, and standard gravity is 80.72 lb. and the generally accepted figure is that air is 23.1 per cent. oxygen by weight. But the air taken in by a blowing engine varies quite widely from 32° F. and 760 mm. pressure and also varies in its moisture content. The equation that applies is $D_1 = D_0 \frac{B_1 - 0.387e}{760} \times \frac{T_0}{T_1}$ in which D_1 is the actual density of the air, D_0 the density of dry air at 32° F. and 760 mm., B_1 the actual barometer reading, e the water-vapor pressure, T_1 the actual temperature (absolute), and $T_0 = 273^\circ$ absolute. Inspection of this formula reveals that D_1 has a minimum value when maximum values of e and T_1 occur simultaneously with a minimum value of B_1 ; or, in other words, the least free oxygen in a cubic foot of air is found on a day when the barometer is lowest, the temperature is highest, and it is raining. Conversely, the most free oxygen in a cubic foot of air occurs on the day when the barometer is highest, the temperature lowest, and the humidity least. It need scarcely be explained that water-vapor pressure is such a function of temperature and humidity that its maxima and minima coincide with maximum and minimum values of those two factors.

In order to get an idea of the range of variability of D_1 let us substitute the observed figures at Pittsburgh, Pa., where so many blast furnaces are in operation.

June 20, 1924, noon; $T_1 = 31.1^\circ$ C. (88° F.); $e = 20.6$ mm.; $B_1 = 738.86$ mm. (29.05 in.).

$$D_1 = D_0 \times \frac{738.86 - 20.6}{760} \times \frac{273}{294.1} = 0.8485$$

Jan. 21, 1924, noon; $T_1 = -17.22^\circ$ C. (1° F.); $e = 0.58$ mm.; $B_1 = 745.48$ mm. (29.35 in.).

$$D_1 = D_0 \times \frac{745.48 - 0.58}{760} \times \frac{273}{255.78} = 1.046.$$

The actual weight of 1000 cu. ft. of free air at Pittsburgh was $80.72 \times 0.8485 = 68.49$ lb. on June 20, 1920; and on Jan. 21, 1924, it was $80.72 \times$

1.046 = 84.44 lb. On June 20, 1000 cu. ft. air contained 0.9 lb. water vapor, which is 88.86 per cent. oxygen by weight; on Jan. 21 it contained 0.03 lb. water vapor. Hence, the weight of the dry air was $83.51 - 0.03 = 83.48$ lb. on Jan. 21; and on June 20, it was $67.73 - 0.90 = 66.83$ lb. The free oxygen content was, respectively, $83.48 \times 23.1 = 19.28$ lb. on Jan. 21; and $66.83 \times 23.1 = 15.43$ lb. on June 20. Adding the oxygen contained in the water vapor, the total oxygen, free and combined, in 1000 cu. ft. of free air at Pittsburgh was 19.3 lb. on Jan. 21, 1924; and on June 20, $15.36 + 0.8$ or 16.16 lb. Taking the mean of these two figures, it is evident that the one is +8.8 per cent. and the other -8.8 per cent. of the mean. Or, putting it another way, there is over 17 per cent. difference between the oxygen content of 1000 cu. ft. of free air at Pittsburgh under summer and winter conditions.

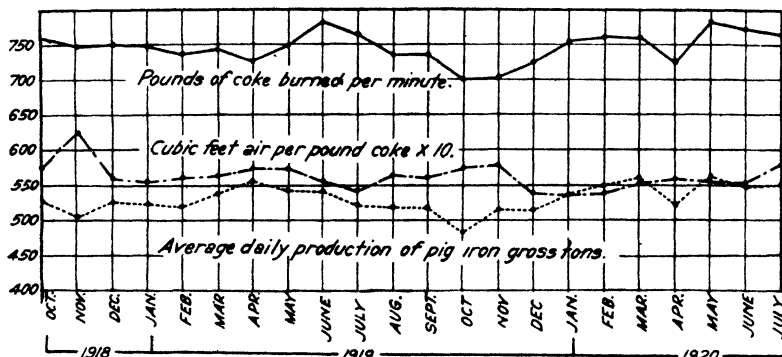


FIG. 1.—AVERAGE PERFORMANCE OF A GROUP OF BLAST FURNACES AT CHICAGO, ILL.

A similar calculation applied to the weather records for Feb. 23, 1923, and July 19, 1923, for Duluth, Minn., where a number of blast furnaces are in operation, gave an even larger variation between winter and summer. The Pittsburgh ranges are more typical of average conditions, however.

It must not be overlooked that about 5 per cent. of the oxygen in the air on June 20 was combined, because the heat absorbed by dissociation of the H_2O is approximately double the heat yielded by burning the oxygen to CO ; or in other words, the furnace is not only getting about 20 per cent. less oxygen per cubic foot of air in the summer than it is in the winter, but about 10 per cent. of what is there is of no value, as far as heat in the hearth is concerned, for 5 per cent. of the free oxygen present is required to balance the heat absorbed in dissociating the water vapor.

The next point to consider is whether, under actual circumstances, such variations may safely be ignored. In Fig. 1, there have been plotted the pounds of coke burned per minute and the cubic feet of air blown per pound of coke burned, as calculated from the data on a group

of blast furnaces at South Chicago.² Inspection of the curves at once reveals that the monthly averages compiled from the records on the individual furnaces show more variation between July and August, 1919, than there is between January and August of that year, in the number cubic feet of air blown per pound of coke burned. Evidently there are other factors influencing the volume of air recorded per pound of coke, and the effects of these are so much greater than the effect produced by variation in the temperature, pressure, and humidity of the air that the effects of the latter are completely masked.

The question may fairly be raised as to whether in the operation of blast furnaces, it would not be a useless refinement to attempt to compensate automatically for variations in the temperature, pressure, and humidity of the air supply of the blowing engines, so that they would furnish a constant weight of air rather than a constant volume. The advantage of so doing would be to eliminate these three variables and permit attention to be concentrated on the other variables mentioned, which would perhaps lead to a better understanding and control of them. In any case temperature, humidity, and pressure of the free air cannot be safely ignored in computing the pounds of oxygen supplied to the furnace from the volume of the air. Calculations based on the pounds of oxygen supplied to the furnace in the blast might be in error as much as 15 to 20 per cent. if the pounds of oxygen are reckoned from the volume blown without correcting for temperature, pressure and humidity, and investigators often base conclusions on observed differences much less than this.

To get the curve in Fig. 1, cubic feet of air have been divided by pounds of coke and the question immediately arises as to the probable error in the measurement of the pounds of coke. At most blast-furnace plants, the only time the coke is actually weighed is in the railroad cars in which it is shipped. On the average, these weights are quite accurate. Railroad scales are inspected and tested by the Bureau of Standards, which reports that, on the average, on a well-equipped railroad the plus or minus error in the scales does not exceed 0.2 per cent. Of course, errors in individual determinations may greatly exceed this, but, in accordance with the theory of probability, such errors of determination should balance each other in a large number of determinations.

Even the tare weight of the car, which is measured at the car shops and stenciled on the side of the car, will not show an average error greater than 0.5 per cent. The tare weight is subtracted from the gross weight of the car and, assuming that the car is completely emptied, gives the weight of the contents quite accurately. In freezing weather, the car may not be completely emptied and some errors may arise from this cause, but it does not seem probable that they would be of much importance except in special instances. The conclusion, therefore, is that the

² W. Mathesius. *Year Book Amer. Iron and Steel Inst.* (1920), 433.

weight of the coke delivered to a blast-furnace plant is determined with a high degree of commercial accuracy.

The coke from the railroad cars is dumped into bins or in storage piles. From these, it is gathered by the charging system and eventually delivered to the furnace in skip loads. The weight of coke charged into the furnace in any given period is obtained by counting the number of skip loads and multiplying by an average figure of the weight of coke per skip. This average figure may be arrived at in a variety of ways; in some places it is changed from time to time by the following method: The weight of coke on hand at the beginning and end of a month is determined by measuring the volume of the stock in the bins or piles and multiplying by an average figure of pounds per cubic foot. The weight of coke delivered during the month is known from the scale weights, and the difference between the weight on hand at the end of the month and the sum of the weight delivered plus the weight on hand at the beginning of the month, should equal the amount charged to the furnaces as determined by the skip loads charged. Actually, these weights do not agree, sometimes by considerable amounts, and they are brought into agreement by altering the weight per skip, as applied to that month. In other words while the volume of the skip is constant the weight assigned to that volume varies from month to month.

The logical basis for this procedure is that everybody knows that the weight of a unit volume of broken material of any kind is variable, depending on the size of the particles with respect to their container, the proportion of different sizes in a mixture of sizes, and a variety of other considerations, such as whether the container has been loosely filled or whether it has been jolted or otherwise compacted. Flagg³ measured the weight per cubic foot of 177 samples of broken coal and concludes "one should not expect that the use of the weights per cubic foot contained in the foregoing table will give accurate results within, say, 10 or 15 per cent. if applied to coal in a storage pile or other place where the material is apt to be in a compact mass." These remarks apply to measures that have been leveled with a straight edge but a skip is not filled to the top, because of spillage. It is probably fair to assume that there is enough probable error in the weight per skip load assigned to the coke to justify altering it to make it agree with the weight as calculated from the stock records. But it should not be overlooked that the two quantities are not endowed with an accuracy they did not previously possess through the operation of being made to agree. Inspection of the curve "pounds of coke burned per minute" in Fig. 1 reveals that its range in the two-years period is plus or minus 5 per cent. of its mean value. It is at least open to question whether the accuracy of the measurement of the pounds of coke burned in any given month exceeds

³ *Weights of Various Coals, Bur. of Mines Tech. Paper 184.*

plus or minus 5 per cent. and if the probable error in the quantities on which the curve is based is as great as the variability of the curve itself; it is not safe to base any inferences on it. For example, comparison of the two curves "pounds of coke burned per minute" and "average daily production of pig iron, gross tons" reveals that they do not keep step, as might have been expected; in other words, an increase in the pounds of coke burned per minute is sometimes accompanied by an increase in pig-iron production, and sometimes by a decrease. A possible inference from this is that there are other factors, not shown, that affect the daily pig-iron production more than the rate at which coke is being burned affects it. This may indeed be true, but the curves do not prove it, because the accuracy of the coke curve is not great enough to justify such use of it.

Turning to the curve "cubic feet air per pound coke," it may be noted that the range of variation of this curve is also within plus or minus 5 per cent., or in other words, the apparent variability of the curve may result from the possible error in the coke weight, on which it is based, rather than from any actual variation in the pounds of air supplied per pound of coke. Here again we do not seem to be justified in drawing any inference from the curve, other than that between 55 and 60 cu. ft. of air are required to burn a pound of coke at this Chicago plant. Using the Pittsburgh figures above as to the range of oxygen in air (from 19.3 to 16.47 lb. oxygen per 1000 cu. ft.) the range in the oxygen supplied per pound of coke burned is from 0.91 to 1.15 lb. if the larger value for oxygen content is applied to the larger volume and the smaller value to the smaller volume. If the smaller value for oxygen content is applied to the larger volume and the larger to the smaller volume, the values become 0.99 and 1.06 lb., respectively; the possible variation in the oxygen content is of the same order of magnitude as the variability of the volume, and by judicious selection of the mean values to be used in calculations they may be made to prove almost anything desired if the probable error in the determinations is ignored.

It is interesting to note in this connection that 1 lb. of coke of 86 per cent. carbon should require 1.15 lb. of oxygen to burn it to carbon monoxide. As all the oxygen of the blast is burned to carbon monoxide in the bosh, it is evident that even the smallest of the four figures given is too large to agree with the determination by Joseph, Royster, and Kinney,⁴ that 77.8 per cent. of the fixed carbon is burned in the hearth, which would correspond to a requirement of 0.89 lb. oxygen in the blast per pound coke. This would indicate that blast furnace records of cubic feet of air blown per minute are probably always in error on the positive side, which might have been expected. The reduction of silica to silicon in

⁴ Royster, Joseph, and Kinney: Reduction of Iron Ore in the Blast Furnace. *Blast Furnace and Steel Plant* (February, 1924).

the bosh region liberates a quantity of oxygen that amounts to less than 0.02 lb. oxygen per pound of coke burned, or about 2 per cent. of the oxygen in the blast, using as a basis the Chicago figures cited above.

In calculations based on the pounds of carbon burned in the furnace, there is not only the possible error in the coke weights, discussed above, but also the variation in the carbon content of the coke. There do not seem to be comprehensive figures on this, but it may be inferred from the figures on the variability of the ash content of coke published by Mathesius.⁵ These show that coke containing 10.8 per cent. ash on the monthly average ranged from under 10.0 to over 11.5 per cent. in the daily average analyses, or a variability of over 15 per cent. in the ash content of the coke. If the variation in the ash content produces an equal variation in the carbon content, this would correspond to about 2 per cent. as the variability of the carbon content of the coke. This is not much, but it adds a complication to the possible error in the weight determinations. The records of the 29 blast furnaces, referred to above, show a range in the average ash content of the coke used from 12 down to $7\frac{1}{2}$ per cent., which indicates the error that may be introduced by using average figures in calculations applying to individual plants.

Another extremely important factor in calculations based on the carbon content of coke is the moisture content of the coke. When the hot coke is pushed out of a coke oven, it is sprinkled with water to quench it. Theoretically, just enough water is used to stop the combustion and the heat of the coke should evaporate any excess water. However, it is extremely difficult to regulate the amount of water as carefully as this and, in addition, the coke, in process of transportation and while stored, is exposed to rain and snow which may cause it to take up quite considerable quantities of water, as the spongy structure of the coke is well adapted to holding large quantities of water by adsorption. In the case of the 29 blast furnaces referred to, some plants do not give the moisture content of the coke and the others report such varying figures as 2, 5, and 12 per cent. This quite variable percentage of moisture in coke introduces another error in the blast-furnace records and calculations, because it is apt to change from day to day. A carload of coke that has been sampled and its moisture determined may take up quite considerable additional quantities of moisture if exposed to rain or snow; and, conversely, coke that is high in moisture may lose a considerable portion of it if exposed to conditions under which the water may evaporate. Where the coke is actually weighed, changes in the moisture content will produce a corresponding change in weight; and where its weight is estimated by volume, change in the moisture content produces a change in the weight that almost defies determination. In the paper by Flag, the second

⁵ W. Mathesius: *Uniform Coking Coal as a Factor in Blast-furnace Economy. Year Book Iron and Steel Inst., New York, (1924) 45.*

conclusion is as follows: "The sample of higher moisture content will usually occupy more space for the same number of pounds of dry coal than will a sample of lower moisture content. However, the increase in volume for the wet coal is not as great proportionately as is the increase in weight per cubic foot." It seems probable that coke of high moisture content will also occupy more space for the same number of pounds than dry coke, but this has not yet been subjected to careful study and accurate determination so that no one can say just what effect variation in the moisture content has on the determinations of the weight of coke by measuring its volume. It is evident, however, that this is a third variable factor in the accurate determination of the weight of carbon actually supplied to a blast furnace. This emphasizes the need of caution in drawing conclusions from curves or calculations based on the weight of coke.

The variability of ash content of coke and of the sulfur content has been so admirably discussed by Mathesius in the paper cited that no further reference will be made to it here, other than to recommend the careful consideration of this paper.

Turning now to the determination of the quantities of iron involved in the blast-furnace process, we have a quite different state of affairs, and one offering even more difficulties. The iron goes into the furnace in a variety of forms. Most of it is in the form of ore, and probably most furnaces use three ores in their furnaces, some four or five. Roll scale, borings and turnings, sintered flue dust, ladle, runner, and ordinary scrap, mixer skimmings, and converter slag, to mention only the principal ones, are charged into the furnace along with ore. The weighing of such material presents no particular difficulty, but its sampling for analysis is exceedingly difficult. The average total quantity so used amounts to about 8 per cent. by weight, of the total iron-bearing material charged, according to the annual statistical report of the Iron and Steel Institute. The scrap and scale are higher in iron content than the ore, some of the other materials are much lower. Where such materials are weighed and an average analysis applied to the weights, the possible error can probably be safely ignored; but in some places, at least, borings, turnings, etc., are thrown on the ore piles or bins, and the weights of some of the other additions are reckoned with a shovel rather than with a scales. The possible error in the quantity of iron charged into the furnace resulting from errors in the reckoning of the material other than ore is probably impossible to determine, but it should be borne in mind in calculations where the quantity of iron is important, or forms the basis of deductions as to furnace performance.

Most of the iron enters the furnace in the form of two, three, or more kinds of ore. Furnaces with modern charging systems usually weigh the ore, so the weights as shown are probably quite accurate. These weights

are multiplied by average analyses applying to each lot of ore. These analyses are usually cargo analyses. The ore as delivered at lower lake ports is sampled by the employes of firms that make a business of such work, one firm representing the buyer and another the seller. At the same time a separate moisture sample is taken. The cargoes range from 3000 to 12,000 tons, and the various samples taken are combined in a single sample and analyzed. The results usually check to 0.5 per cent. on the iron, representing a probable error of 1 per cent. in the amount of iron present. This represents the agreement of two samples taken by the same general method under the same conditions. No one knows, or can know, how closely the samples represent the actual average composition of the lots of ore sampled. Through the courtesy of some of the operators the author has obtained the carload analyses, made at the mines, on four cargoes, ranging from 4000 to 10,000 tons. These compare as follows:

IRON, PER CENT.

Cargo number.....	I	II	III	IV
Cargo analysis No. 1.....	56.90	54.29	37.09	36.45
Cargo analysis No. 2.....	57.23	54.45	36.38	35.39
Carload analyses, average.....	(44) 56.25	(25) 52.50	(72) 37.45	(102) 36.71

The figures given are the percentage of iron, natural; or, in other words, the percentage of iron in the dried sample has been calculated back to the percentage of iron in the natural sample by allowing for the percentage of H_2O shown in the moisture samples, which was as follows:

MOISTURE, PER CENT.

Cargo number.....	I	II	III	IV
Cargo analysis No. 1 ...	7.78	7.67	20.71	20.58
Cargo analysis No. 2....	7.09	7.34	20.91	19.62
Carload analyses, average..	(14) 8.87	(8) 9.60	(25) 16.90	(27) 17.61

The numbers in parentheses beside each carload average, in both tables, are the number of determinations that have been averaged to give the analysis shown.

Inspection of these tables indicates that calculations of the actual weight of iron are probably correct to within 1 per cent. as far as the iron percentage is concerned; but as the weights of ore delivered to the furnace must be corrected for moisture, and as the moisture figure does not seem to be reliable within 10 per cent. of the quantity found, the probable error in calculations as to the total weight of iron charged into the furnace in the form of ore is likely much larger than 1 per cent. There seem to be quite considerable differences in the moisture content at the mine and at lower lake ports, and the differences between the ports and the blast-furnace skips are conceivably equally large.

A factor that has so far been overlooked is the relative magnitude of the quantities to which the averages are applied. This can be most clearly explained by the use of analogy. Suppose a regiment of 2400

men, divided into companies of 200 men each. The average height of the regiment is 5 ft. 8 in.; the individual men range in height from 6 ft. 2 in. down to 5 ft. 2 in. If care is taken in assigning the men to the companies they can be so arranged that the average height of each company will also be 5 ft. 8 in. or very nearly. Now suppose 10 men, taken at random from a company, are told to report to the captain. The average height of these men would not be 5 ft. 8 in., they might be all 5 ft. 2 in. men or they might be all 6 ft. 2 in. men. If the number of 5 ft. 2 in. men in the 200 men is known, it is quite simple to calculate the probability that 10 men taken at random from 200 men would average 5 ft. 2 in. By similar methods, using the height of each man, the number of men, and the average height, it can be calculated that 10 men taken at random from 200 men would not show an average that would differ from the average of the 200 by more than the amount revealed by the calculation. If each of the 200 men was 5 ft. 8 in., then the average of 10 men taken at random from the group would differ from 5 ft. 8 in. by zero, but if some of the men were shorter, and some taller, the average of 10 men taken at random might differ from the group average by an amount that would be a fraction of the amount the individuals differed from the average.

Another way of expressing this is to say that an average only applies to the number of quantities of which it is an average. If a fractional part of the group averaged is taken that fraction may differ from the group averaged by a quantity which is a fraction of the number in the group, the number in the fraction, and the extent to which the individuals differ from the group, or their variability.

Applying this example to the case before us, iron ore as dug from the pit is loaded into a car, which is sampled, and thus constitutes an individual lot. The individual cars are dumped into the pockets at the ore docks in such a way as to make the average for the pocket come as near the average to be shipped as is practicable. It is generally believed that the operations of sliding the ore down a chute into the vessel, digging it out of the vessel at the lower lake port, loading it into cars, and dumping these cars into bins or storage piles at the furnace plant mixes the ore from the individual cars so that the product delivered at the blast furnace is quite uniform in composition. So far as I know, no test has been made to determine whether such mixing actually does take place. Experience indicates that when a mixture of coarse and fine material is allowed to roll or slide the coarse and the fine tend to separate, and if they differ in composition the resulting piles are less uniform, instead of more uniform, than they were before the material was moved. Without making a test, it is impossible to say whether any individual one-tenth part of an ore pile at a blast-furnace plant would differ, and how much, from the average of the pile as indicated by the analysis of the cargo of which it formed a part.

In the light of this discussion, it seems probable that the possible error in the calculations of iron charged to a furnace, based on furnace weights and average cargo analyses, will be of the order of magnitude of 5 or 10 per cent.

Silica enters the blast furnace in the ore, the coke and the limestone; usually nearly three-fourths of the silica is in the ore, about one-fourth in the coke, and about one-twentieth in the limestone. The variability of ash in coke is quite thoroughly discussed in the paper by Mathesius, and coke ash is usually about 50 per cent. silica. The calculation of the silica entering the furnace with the coke would not only be affected by the variability of the silica content of the coke, but by the possible error in the determination of the weight of the coke, which has been discussed above. It seems unlikely that calculation of the silica entering the blast furnace in the coke can be counted on to be accurate to within 5 per cent.

As only about 5 per cent. of the total silica involved in the blast-furnace operation enters with the limestone, a 10 per cent. error in the limestone weights or in the agreement between the actual analysis and the average figure used would only affect the total by 0.5 per cent., therefore this possible error may, in most instances, be safely ignored.

About half of the total silica enters the blast furnace with the ore. It has already been pointed out that while the weight of ore charged into the furnace is quite accurately determined, this weight is the "natural" weight, and the dry weight, which is used in calculations, may be affected by a considerable error that may be introduced by the possible error in the moisture averages. The actual moisture in ore has been shown to be sufficiently variable to cast considerable doubt on the accuracy of average figures as applied to the ore charged in a given period. Some of this doubt arises because the determinations on individual lots differ enough from the average of a group of lots, such as a 10,000-ton cargo, to make it probable that when individual lots taken at random are charged to the furnace the average of those lots may differ by an unknown degree from the group average, but most of the doubt arises because of the possibility of fluctuations in moisture content between the time of sampling and the time of weighing. Ore that is being removed from a pile in a rainstorm or snowstorm will undoubtedly increase in moisture content. On the other hand, in a hot dry spell if the ore is being removed from the pile at a rate that permits the surface layers to dry out, from the effect of the sun and wind, decrease in moisture content will result. It has been pointed out that ore standing in a bank for a long time does not show any marked decrease in moisture content as compared to the average for that orebody, but it should be noted that ore only dries out on exposed surfaces, and the exposed surface in a bank is very small compared to the exposed surface of ore in a pile. The change of moisture content of ore in handling and on exposure is affected not only by weather conditions,

but by the texture of the ore and the total moisture present as well. Generalization seems impossible and it is only by actual investigation in specific instances that safe inferences can be drawn as to the probable effect that error in average moisture figures may have on the calculation of dry weights of ore.

Another point that requires equally serious consideration is the probable error in the average silica content of the ore. In the case of the four cargoes of ore already referred to the silica determinations compare as follows:

PER CENT. SILICA IN IRON ORE

	Cargo I		Cargo II		Cargo III		Cargo IV	
	Dry	Natural	Dry	Natural	Dry	Natural	Dry	Natural
Cargo analysis No. 1...	7.84	7.23	9.74	8.99	6.18	4.90	5.74	4.56
Cargo analysis No. 2...	7.30	6.78	9.15	8.47	5.90	4.66	5.98	4.81
Carload analyses, average.....	(44) 7.87	7.17	(25) 10.49	9.48	(25) 6.08	5.05	(27) 5.97	4.91

Considering the "natural" averages (the dry percentage corrected for the amount of moisture present), there are differences as great as 0.5 per cent.; in one case the difference is 0.99 per cent. According to which of the figures is taken as the average figure, the total silica as calculated from them will vary 8 to 10 per cent. of the total amount present. This is not the whole story, however. Inspecting the analyses of carload lots, of which from 25 to 44 (as indicated by the figures in parentheses) have been averaged, shows that they differ even more widely from one another:

PER CENT. SILICA DRY, MINE ANALYSES

Cargo number.	I	II	III	IV
Number of analyses.....	44	25	25	27
Average percentage	7.87	10.49	6.08	5.97
Average difference.....	1.69	1.39	1.08	0.99
Maximum difference.....	6.33	4.72	2.48	2.44

The weights to which the individual analyses apply range from 100 to 400 tons. It is evident from these figures that ore as shipped varies a good deal in its silica content; one lot in cargo No. 1 differed from the average by 85 per cent. of the average value. It therefore follows that not only will the actual composition of a fractional part of the quantity to which an average figure applies differ, perhaps to a considerable degree, from the average but the average figure itself is likely to be considerably in error because of the practical difficulty in obtaining a true sample of material that varies a good deal in its composition. This is a difficulty that is quite well known to gold miners; it is a matter of record that a \$12,000,000 gold mining enterprise resulted in failure because the true

average of the gold content of the ore, as revealed by mining, was only about two-thirds of what had been expected from the operations of a 75-ton per day mill, on what was believed to be average ore, for nearly two years. The average moisture and silica content of iron ore are undoubtedly the least reliable figures of any (other than volume of air blown) involved in blast-furnace calculations, and any calculations that involve their use (and many do) should be regarded as involving large possible errors.

Of the other substances involved in blast-furnace operations, it scarcely seems necessary to speak, for the general considerations set forth in regard to the carbon, iron, silica, and moisture can easily be applied to the CaO , Al_2O_3 , MgO and other components, with a due regard for the special circumstances that apply to each. Sulfur may be specially mentioned because, although the quantity involved is small, it produces, like a fly in a glass of milk, an effect entirely out of proportion to its actual mass. Joseph⁶ has made a careful inventory of the sulfur in charcoal and coke blast-furnace operations and finds that in coke practice 92 per cent. of the sulfur enters with the coke, 7 per cent. with the ore, and 1 per cent. with the stone, while 87 per cent. of the sulfur goes off in the slag and about 5 per cent. enters the pig iron. This accounts for 92 per cent. of the sulfur without tracing the unknown amount that goes off in the gases from the furnace. Everything considered, this seems to be as close a check as could be expected, and the figures given are the more significant because they do not exhibit an apparent mathematical exactness that such figures do not, and cannot possibly, possess. Unless blast-furnace operations are studied in the light of the probable accuracy of the records and of the calculations based thereon, truly scientific interpretations of the blast-furnace processes seem hardly possible.

To summarize, it has been set forth that nearly every measuring operation involved in securing blast-furnace records involves a possible error of 5 per cent. or more, and quantities that are commonly measured with greater accuracy than this have to be multiplied or divided by figures involving a possible error of 5 or 10 per cent., thus introducing a corresponding possible error into the quotient. In interpreting curves or tabular summaries, the possible error should be always kept in mind, and observed differences that do not greatly exceed the possible error of the data should only be used with caution in drawing inferences and deductions as to the blast-furnace process.

It must not be inferred from the foregoing that since blast-furnace records show determinations made with only as high a degree of commercial accuracy as practical considerations of expense permit, and must be interpreted in the light of the probable errors involved, they are

⁶ T. L. Joseph: Effect of Sulfur on Blast-furnace Process. *Trans.* (1925) 71, 453.

therefore not a valuable guide to blast-furnace operation. A good example of a similar case is the taking of a patient's temperature by a physician as a guide to diagnosis and treatment. Such temperatures are usually taken with a thermometer graduated to 0.2° F. and (for a variety of reasons) the temperature thus recorded is probably not within 0.5° F. of the actual temperature of the patient. The significant range of body temperature is only 10° F., and the possible error is therefore 5 per cent. of the significant range. This does not discredit the general method; it merely reduces the importance to be attached to minor apparent fluctuations. Similarly, blast-furnace records are valuable for the purpose for which they are intended, but when they are made the basis of calculations of a high degree of mathematical accuracy it must not be forgotten that the possible error in the original figures may be large enough to invalidate entirely conclusions that might otherwise be drawn from the calculated results.

DISCUSSION

C. H. HERTY, JR., Boston, Mass.—The author stresses the point that the air blown in the furnace is variable. We have made some tests on the gas analysis, calculated it back to the blowing engine for a number of types of engines and have found that the error was somewhere between 8 and 12 per cent. By a simple gas analysis test and the specifications of the blowing engine you can calculate the difference between the blowing engine and the air actually entering the furnace and can eliminate that error almost entirely, because tests for two or three months show almost the same figures for those periods.

T. T. READ.—Did you find that the difference was always a plus difference?

C. H. HERTY, JR.—Absolutely; we calculated 40 and the engine would say 46.

T. T. READ.—Can anybody explain why these blast-furnace records show an apparently nearly uniform volume of air supplied per pound of coke burned in this Table 1, whereas we know that the oxygen content of a cubic foot of air varies considerably between winter and summer?

C. H. HERTY, JR.—Is it not true in the summer time that you increase the speed of the blower?

T. T. READ.—I simply took the cubic feet of air blown according to the published records.

T. L. JOSEPH,* Minneapolis, Minn.—We all recognize that the amount of air required to burn a pound of coke varies from furnace to furnace, and may vary on a particular furnace because the amount of carbon reach-

* Metallurgist, Bureau of Mines.

ing the tuyeres varies over quite a wide range. In other words, part of the carbon is absorbed by "solution loss" or it may be picked up by direct reduction; consequently a smaller amount of carbon will reach the tuyeres and will require in turn a smaller amount of air. Furnaces in this country are operating on coke, which is almost like charcoal in strength and reactivity with carbon dioxide. Less air is required to burn a soft coke than a hard coke, which will not be absorbed by the carbon dioxide in the top part of the furnace.

R. H. SWEETSER,* Columbus, Ohio.—It is usual, in blast-furnace practice, to keep records of the amount of air blown reduced to 62° temperature, and every rise of 10° in the outdoor temperature means a reduction of 2 per cent. in the amount of oxygen. In some blast-furnace plants, the engineer will have on the outside of the engine room a wet-and-dry bulb thermometer and he will have instructions that when the temperature goes to 70°, he will automatically increase the engine speed so as to give approximately the same weight of oxygen; if the furnace will not drive on that amount, the superintendent will take other steps to have about the same amount of oxygen going into the furnace per minute.

It is good practice to have a balance sheet for the blast furnace not only for the air but for the coke; if it is found that the amount of air reported per pound of coke varies too much above 56 cu. ft. something is wrong, which must be determined.

The weight of coke charged to a blast furnace is the railroad weight, because that is the weight that determines the cost of pig iron. This railroad weight is checked up, at least weekly, with the amount of coke in volume that is going into the blast furnace, and that can be very easily balanced. It is also good practice to have a balance sheet for the amount of ore that goes into a blast furnace. If there is any one thing that is analyzed carefully, it is iron ore—not only at the mine itself but at the dock where it is mixed; most ores now are mixed. Then the ore is analyzed again at the lower Lake points, and nearly every blast furnace will also analyze the ore as received, so that the actual units of iron going into the blast furnace are quite accurately known. At the end of the month, a balance sheet shows how many units of iron have gone into that furnace and a balance sheet shows how much has gone out as pig iron, as iron in the slag, and as scrap; or where you have direct metal how much has gone out with the kish, which is deducted at the open hearth; and then there is that "unaccounted-for loss." If the superintendent gives more than 100 per cent. return, you must look for the cause. It is part of my duty to find out where those things go, and in one blast furnace that I went over not long ago I found out that 220 tons of scrap had been

* Assistant to vice-president, American Rolling Mill Co.

recovered from slag and put back through the furnace without being charged into the cost of it. The man had produced that iron, lost it in his slag, and later recovered it. In an up-to-date blast-furnace plant, records are kept much more accurately than one would suppose by reading this paper.

The author has done something good for the blast furnace just as Mr. Feild did 8 years ago when he visited several of the blast-furnace plants to find out the composition of slag. He called attention to the fact that the sampling and the analyzing of the slag were very carelessly done, and he brought about some reforms that most blast-furnace men have taken advantage of, and I think that most blast-furnace men will now take advantage of the author's study.

T. T. READ.—Errors in the iron balance of the blast furnace, while important to the operator, are not what I was most interested in; my attention was concentrated principally on the silica. As pointed out in the table, there is sometimes a difference of 10 per cent. between two equally authoritative analyses of the ore. If one analysis is right the other is 10 per cent. in error and this naturally leads to a doubt as to whether either is within 5 per cent. of the actual amount of silica in the furnace burden. When attempting to use these records of what happens in the blast furnace, we are confronted by the fact that the range of conditions in different blast furnaces is rather limited, and in attempting to determine the relation between coke and silica by plotting them against each other one is in much the same position he would be if he plotted the age and height of children against each other, using only children between 10 and 12 years of age. Everyone knows that some children 10 years old are taller than some 12 years old and working in such a narrow range one would not be able to detect any significant relationship between age and height, whereas if he plotted age against height over an age range between 2 years and 20 years a relationship between age and height would become evident. A 5 or 10 per cent. error in the weights of coke and silica, as shown by the records, has the same effect on the curve as the natural differences in height of children of the same age, and unless the actual weights are determined very accurately it is difficult to draw curves of blast-furnace performance that can be relied on as indicating the actual relationship between the substances involved.

For the purpose for which they are principally kept, blast-furnace records are sufficiently accurate; when, however, one attempts to use them for purposes for which they were not intended, such as making accurate mathematical calculations as to the relationship, he may be easily lead astray unless the probable error is kept in mind.

Making Rimmed Steel

BY CARL PEIRCE,* MANSFIELD, OHIO

(New York Meeting, February, 1926)

THE writer of this article has not attempted to write a technical paper; on the contrary, he has tried to express in "steel-plant English," for steel men, a viewpoint drawn from his practice and experience. It is not his thought that it shall be taken as the "last word" in the making of this class of steel, or that good rimming steel cannot be made by any other practice. The paper was written to serve as the basis of a discussion from which it is hoped much benefit may be derived.

The paper deals only with rimming steel made by the open-hearth process, and with the lower carbon steels, such as sheet and tin bar, rivet stock, skelp, etc., although good rimming steel as high as 40 to 50 carbon can be made by having good open slags and giving proper attention to working and tapping temperatures.

DEFINITION OF RIMMED STEEL

Rimmed steel is sometimes called open or effervescing steel to differentiate it from killed or partly killed steel. It is steel made by a process which permits the free escape of gases from the metal in the molds. In passing up through the metal, the gases keep it in a rolling action from the walls of the mold inward. The top of the ingot rims in as the metal chills and the walls of the ingot get thicker, the center part remaining fluid until it reaches a pasty condition when it is covered with a cast-iron cap.

THE CHARGE

In making up a charge for rimming steel, clean stock of a known composition must be selected, special attention being given to the analysis of the materials. The silicon in good rimming steel must be eliminated to a trace, therefore it is advisable to have a uniform amount going into the charge. Too much silicon gives a raw melting heat from which rimming steel is unlikely to result. For this reason a charge containing not to exceed 40 per cent. pig iron and 60 per cent. scrap, with no iron ore, is preferred to the Monell type of charge in which as high as 65 to 70 per cent. pig iron is used with a proportional amount of iron ore for the removal of the excess silicon and carbon. The silicon content of pig iron varies so much from day to day in the average blast-furnace practice that there is danger of getting too much of this element in the latter mixture when

* With Mansfield Sheet & Tin Plate Co.

using the output from a battery of blast furnaces. The writer, when working in a plant that used a 65 per cent. pig iron charge, has often seen the metal in the mixer carrying more than 2 per cent. silicon when the limestone in the charge was fixed to care for 1 to 1.25 per cent. silicon iron.

The smaller the amount of pig iron in the charge (consistent with having the heats melt high enough for proper working), the less chance there is of having raw melting heats. Good clean scrap should make up the steel part of the charge. A sufficient amount of limestone should be used to give mushy slags when boiling loose from the bottom. If the stone comes up in hard lumps and the bath looks raw and red, there is too much silicon-carrying material for the amount of limestone charged. By using a mixture of clean materials, good rimming steel can be made with a limestone charge of 8 per cent. The general practice, however, is to use about 10 per cent. Enough pig iron should be charged to have the heats melt between 40 to 80 per cent. carbon, although it is better to have them melt too high than too low. The serious effects of having heats melt soft is not given enough consideration by the average open-hearth melter.

In the year 1914, in an open hearth in which it was the practice to charge the heats to melt close, a report was made to the superintendent covering all rail heats (1338 in number) made during a period of seven months. Rail heats were used as a basis because on this class of material it was possible to get an accurate record of the faulty material produced. This report showed that heats which melted soft averaged 7.1 per cent. second and condemned rails as against 4.2 per cent. second and condemned rails of those using ore in the working. Heats that melted close—that is, using neither ore nor extra metal—averaged as high in faulty rails as those that melted soft, because the furnacemen handle their furnaces in the same way in both cases. It often happens, in large open hearths, that when a heat is melting low, the furnaceman waits until the carbon is down to 0.15 per cent. or below before ordering extra metal. As he frequently has to wait half an hour before getting it, if the heat happens to be losing carbon particularly fast, it is dead soft by the time the extra metal reaches him, and the bath is in exactly the condition of an overblown Bessemer heat.

Several years ago, the writer asked a helper to show him the test on which he ordered his “drink of metal.” The testpiece showed the carbon to be nearly gone. At tapping time, the heat was in particularly fine shape, a close tapping temperature, creamy slag, and a testpiece with a tough silvery fracture. When the writer expressed the opinion that the heat might not roll well, the furnaceman was indignant. At the rail mill it was said to be the worst heat of the day, finishing 9.1 per cent. second and 1.4 per cent. condemned rails.

In both Bessemer and open-hearth processes, the method of manufacture is an oxidizing one, advantage being taken of the great affinity of the

impurities in the steel for oxygen. Low carbon steel cannot be made by either process without overoxidizing the metal; that is, increasing the amount of ferrous oxide in it. At high temperatures the affinity of iron for oxygen is greater than carbon for oxygen. As proof of this statement, E. Von Maltitz¹ gives the following apt illustration:

If from a heat high in carbon but low in temperature, a small sample is poured into a test mold, the steel will solidify quietly. It will not sputter and will not show any blowholes when broken. But when a similar test is taken from a heat of practically the same carbon content but of a much higher temperature, the steel will be wild, will sputter and rise considerably and when broken will show many blowholes. In the first case, although ferrous oxide was certainly formed continuously in the bath, the metal refused to dissolve it, and the carbon having a greater affinity for oxygen than iron immediately reduced it. Hence the metal poured into the mold did not contain ferrous oxide and the formation of carbonic oxide in the solidifying steel being impossible, the steel set quietly without forming blowholes. In the second case, however, the much higher temperature of the bath increased the solvent power of the steel for ferrous oxide, while on the other hand the affinity of carbon for oxygen was becoming less than the affinity of iron for oxygen. The rapidly sinking temperature of the steel in the mold approaching the freezing point reverses these tendencies; a large amount of carbonic oxide is set free which liberates hydrogen and nitrogen which becomes entangled as it passes through the pasty condition of the metal and forms blowholes.

The theory that at high temperatures the affinity of carbon for oxygen is less than that of iron is sound, most open hearth men will attest, since it is well known that it requires more ore to reduce a given amount of carbon when the bath is very hot than when it is on the cool side.

WORKING THE HEAT

Few steel men realize how the manner of working affects the quality of the steel. They have a vague sort of idea but as a rule no definite information. In compiling the data for the report on heats melting soft, several very interesting points developed, one of them being on this subject. One furnace was selected where the helpers were noted for the high temperature they carried when working their heats. One day, one of these helpers was seen to pour a spoonful of high-carbon metal on the floor before starting to ore the heat, and on being asked why he did this, said it was to see whether it was hot enough to take the ore. By way of comparison, another furnace was chosen where the helpers worked their heats on the cold side, had open creamy slags and a close temperature when ready for tapping. Both furnaces were of the same size, used the same charge, and were tapped by the same melters. Table 1 (page 1029) shows lists of consecutive rail heats made during the same period on these two furnaces. The second and condemned rails of the first furnace averaged almost six times those of the second furnace.

When starting to work a heat, ore should not be added until the limestone is practically all loose from the bottom and the air and gas should

¹ Blowholes in Steel Ingots.

TABLE 1.—*Rail Heats Made on Two Furnaces*

Furnace No. 1		Furnace No. 2	
Seconds, Per Cent.	Condemned, Per Cent.	Seconds, Per Cent.	Condemned, Per Cent.
22.1	3 5	0 0	0 7
5 8	0 0	0 0	0 0
2 1	25 7	0 0	0 0
13 3	2 8	0 0	0 0
1 6	0 0	0 0	0 0
1 4	0 0	0 0	0 0
7 4	0 7	3 1	0 0
0 8	1 5	1 1	0 0
2 5	0 0	1 2	0 0
0 7	0 0	1 8	0 6
3 3	2 6	3 5	0 6
15 0	2 5	0 0	0 6
8 3	3 0	5 3	0 0
3 0	1 5	2 7	0 0
14 2	0 7	1 9	1 9
3 3	0 0	3 3	0 8
5 3	0 0	4.4	0 9
22 6	11 3	0 0	0 0
0 8	0 8	0 0	0 0
0 0	0 7	0 8	0 0
2 3	0 8	0 0	0 0
14 5	0 0	1 5	0 0
13 0	1 5	0 0	0 0
4 3	0 7	1 2	0 0
8 3	0 6	3 6	0 6
1.7	0 6	0 7	0 0
1 3	0 0	0 0	0 0
13 9	2 9	0 0	0 0

be cut back to keep the metal from getting too hot because of its increased capacity for picking up gases when at a high temperature. In the making of low-carbon steels, the heats should not be ored below 0.20 to 0.25 per cent. carbon, that remaining being barely sufficient for shaping the slag and giving the bath the proper amount of stirring to rid it of its excess gases. As raising the temperature of steel increases its capacity for absorbing gases, so decreasing it aids the steel in throwing them off. The throwing into the bath of cold scrap, pig iron, the stirring with a rod, even the addition of molten manganese or spiegeleisen, because of its lower temperature aids in this liberation. That the gas escaping is chiefly carbon monoxide from the reduction of ferrous oxide by carbon is probably true; after a bath has been stirred with a rod, the carbon is considerably lowered.

The use of a half-box of pig iron while shaping the slag materially improves the quality of the steel. The argument may be brought up that this procedure will lengthen the time of the heat one-half hour. Standard open-hearth practice shows an hourly output of 6 to 8 tons and when a box of pig iron of 5000 lb. is melted and converted into steel in one-half hour, the furnace is making steel at a 4-ton per hour rate. If the rate of the furnace is 7 tons per hour, an actual loss of $1\frac{1}{2}$ tons of steel, or 13 min. of time, has been consumed by this practice. The use of a box of pig iron not only aids the steel in getting rid of its injurious gases but its action in the bath helps in dissolving small pieces of lime, which ordinarily would be deposited on the hearth when the heat is tapped, so that in the long run less bottom trouble would be experienced by this practice and the improvement in the quality of the steel should more than compensate for the apparent loss of tonnage.

SHAPING THE SLAG

During the oreing process, iron oxides are brought into the bath, which gives the metal every opportunity to saturate itself with ferrous oxide. To prevent too high a degree of oxidation during the working of the heat, the temperature of the bath must be controlled, also the oxidizing influence of the slag. If a heat is finished with a slag too rich in oxygen, ferrous oxide is likely to be transferred from the slag to the metal up to the last moment before tapping. If the bath is very hot the metal has a greater solvent power for ferrous oxide regardless of the carbon content.

In the making of low-carbon steels, such as sheet-bar, skelp, etc., great care must be given to the shaping of the slag. If the heat has been worked down cold and no spar has been added until the last ore addition has worked through, no difficulty will be experienced in attaining a satisfactory pouring temperature. Fluorspar should be used very sparingly; the shaping of the slag and the raising of the bath to the final tapping temperature should be carried on together. A creamy slag rather than one too heavy or too thin, with plenty of action to the bath, will give the best rolling practice for the steel.

CASTING TEMPERATURE

In either top or bottom pour, the steel should be hot enough to pour cleanly. In soft steel top pour, a temperature that will leave a flat saucer skull in the bottom of the ladle is the ideal one; in bottom-pour practice, the steel must be hotter than this, for in most groupings the steel will not rise evenly in the molds, and some butts will be made if it is cold enough to leave a saucer skull in the ladle.

Many open-hearth men feel that the best quality of steel is obtained when the heats are tapped so that a fair-sized skull is left in the ladle.

Recently, the writer went over some cards of heats cast in an open hearth following this practice. Of 29 heats, 7 were reported as having no skulls; 2 had skulls of 500 lb. each; 9 had skulls from 1000 to 2500 lb. each; 11 had skulls from 3000 to 12,000 lb. each. Some of the cards had no notation as to how the heats poured, so it is taken for granted that their pouring was good. Some of the cards showed the following notes: Used pricker on the fifteenth mold; running stopper from the sixth mold through the balance of the heat; pricker on the first mold, oxygen on the second; sloppy pour; heavy drip; running stopper two molds; heavy drip on balance.

A heat tapped on the cold side evidently is worked the same way, and it is possible that some of the credit for quality given to the fact that the heat has been tapped cold should be given to the fact that it was worked cold. The average of a large number of heats would probably show that if they were worked on the cold side and then tapped just hot enough to guarantee clean pouring, the quality of the steel would be better and the yield and general practice much improved. In the larger open hearths, making 60,000 tons or more per month, if three extra melters were added to the force, and each melter given supervision of the steel made on not more than four furnaces, so that proper attention could be given to the working and tapping temperatures on each furnace, the extra cost would be less than two cents per ton on the conversion cost, and this could be saved many times by the better quality of the steel and the more satisfactory charging and operation of the furnaces.

POURING

Many heats of well made steel are spoiled by improper handling in the casting pit. In the teeming of top-cast steel, the stopper should be opened slowly until a body of metal (3 to 4 in.) has accumulated in the bottom of the mold. This can take the full force of the stream without splashing, but if the full force is applied without this precaution metal is splashed one-quarter or one-third the way up the walls of the mold. The thin shell formed by the splashing chills before the molten metal reaches its top and a proper union cannot take place at this point, so that small cracks develop when the ingot chills and form seams and tears in the finished bar.

METALLURGY OF RIMMED STEEL

In the manufacture of rimming steels, it is necessary that certain elements be present in order to produce the rimming action in the molds; it is also necessary that other elements which prevent or hinder this action should be removed.

The gases which form the blowholes found in all rimmed ingots are classified by Henry D. Hibbard as follows:

(1) Hydrogen, which forms the long blowholes found in the lower half or third of the ingot, which grow as the metal chills and develop in the line of least resistance, toward the center of the ingot. This is the long pencil-like type of blowhole which gives the spongelike appearance to the skin and which in many top-cast ingots makes the lower half appear much darker in color than the top half when it is stripped. An ingot with this kind of skin will tear and crack under the action of the rolls and produce a scabby and seamy bar, unfit for most purposes.

(2) Carbon monoxide, which causes the second type of blowholes. These are round in appearance and in good rimming steel are located in a line just under the skin.



FIG. 1.—FRACTURE OF AN IMPROPERLY-MADE RIMMED INGOT. NOTE THE LONG HYDROGEN-FORMED BLOWHOLES IN THE OUTER SKIN OF THE INGOT.

(3) Nitrogen and ammonia, which cause the third class. These also are spherical in shape; they are found in the central part of the ingot.

The blowholes of the last two types are practically harmless, those caused by hydrogen being the harmful ones. Fig. 1 shows the fracture of an ingot which may have been cast at a very high temperature or have been worked with the bath very hot, so that the bath boiled very mildly; or it may have melted soft, having no boil at all, and consequently the bath contained more hydrogen than it should.

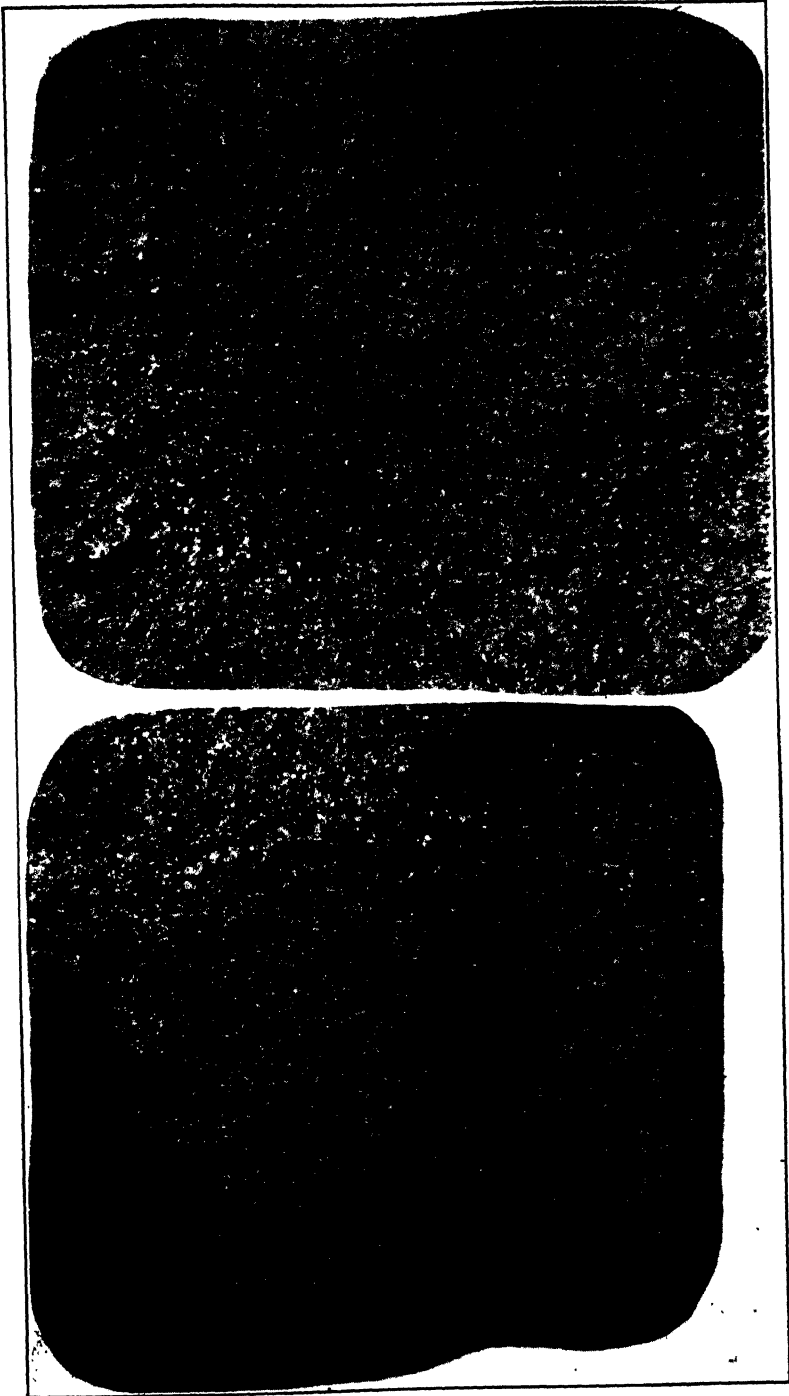


FIG. 2.—FRACTURE OF A BOTTOM-CAST RIMMED INGOT, 15×17 . THE BLOWHOLES BENEATH THE SKIN WERE FORMED BY CARBON MONOXIDE.

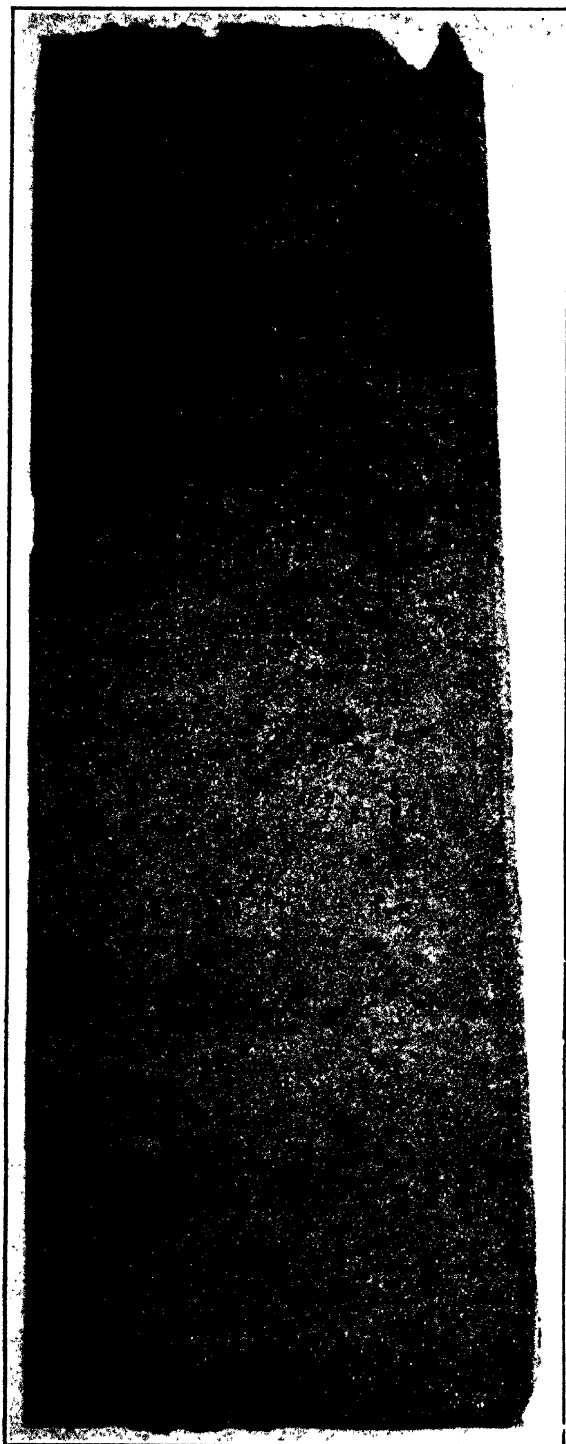


FIG. 3 — SPLIT TOP-CAST RIMMED INGOT, 15 X 17.

The theory of rimming steel is that carbon monoxide is the element that keeps the metal in an open boil and which, in escaping from the steel, carries off with it a considerable portion of the hydrogen, both that which is dissolved in the metal and that which has begun to collect in bubbles clinging to the freezing walls and which is unable to escape by itself. (Fig. 2.) It probably carries off some of the nitrogen as well. The proper rate of their evolution is such that the steel does not rise as it solidifies and the ingot has a flat top when frozen. The writer is not averse to having the steel settle as much as 4 in. when rimming, as this guarantees ingots with a minimum number of hydrogen blowholes in the lower third of the ingot. The casting temperature and the rapidity of pouring have a great effect on the evolution of these gases. When it is far too hot there may be no evolution and the metal rises in the molds because of the displacement by the blowholes formed in the skin of the ingot. If the steel is overoxidized and the carbon is very low, often the gas will escape and leave a boot-leg at the top of the ingot, showing that the gases formed half of the volume of the steel in the mold.

Fig. 3 shows a split top-cast rimmed ingot.

Silicon in the open-hearth bath protects the carbon from oxidation and lessens the vigor of the boil. In protecting the carbon from oxidation it limits the amount of carbon monoxide formed, ample supplies of which must be allowed to remain in the metal to give the desired action in the molds.

As a rule the amount of carbon the bath contains at the time of tapping governs the amount of carbon monoxide in the bath; the lower the carbon, the greater the amount of carbon monoxide present. Since in rimming steels the thickness of the skin of the ingot depends on the length of time it takes to rim, and this rimming effect is caused by the carbon monoxide present in the steel, it follows that the rimming action will last longer and the heats will be more uniform if they are tapped on the lower limits of the carbon specification. For sheet and tin bar, 0.08 to 0.10 per cent. carbon is preferred to a 0.10 to 0.13 per cent. carbon specification, as the steel is less likely to rise in the molds, it will take a longer time for rimming and produce thicker skinned ingots. There is also less trouble with segregation in the lower carbon ranges.

In good effervescing steel, the amount of manganese added greatly diminishes the volume of carbon monoxide in the metal, hence diminishes the amount of hydrogen swept off by the rising CO bubbles. This is accomplished by the manganese decomposing the carbon monoxide with the formation of oxide of manganese, the liberated carbon being dissolved in the metal. So when the carbon monoxide is decomposed and therefore cannot cause effervescence, and no solvent for the hydrogen is present, skinholes are formed and the steel rises in the mold. For this reason, in this class of steel, the keeping of the manganese near the low limit of the specification, around 0.30 per cent., is favored.

Aluminum should be used very sparingly—from 2 to 5 oz. per ton of steel with the preference for the low limit. It should not be used in the molds unless absolutely necessary.

SUMMARY

1. In making good rimming steel, materials of a known composition must be used and a satisfactory mix made, enough pig iron being charged to guarantee that the heats will not melt soft.

2. Most important. Special attention must be paid to working and tapping temperatures, to shaping the slag and to slow pouring.

3. Steel must not be overoxidized but must contain a sufficient amount of carbon monoxide to produce the rimming effect.

4. In the finished steel, silicon must be down to a trace, and for soft steel, 0.08 to 0.10 per cent. carbon and 0.30 to 0.35 per cent. manganese is preferred.

DISCUSSION

J. VANICK, Bayonne, N. J. (written discussion).—The presence of ammonia in the steel, originally, is doubtful, as some one has remarked in the discussion, but it is true that the odor of ammonia may be detected in the vapors rising from the ingots. The ammonia so detected probably comes from sources external to the ingot during cooling, since ammonia would be dissociated at temperatures above 600° C. Steam in the molds or water vapor in the air would supply the hydrogen while nitrogen would also be more likely to be cracked from the envelope of air around the ingot. The hot iron would operate as an excellent catalyst in assisting in the union of nitrogen and hydrogen, the iron going to oxide. The alkaline earths from slag inclusions, molds or ladle linings would promote such a reaction. For example, the odor of ammonia may frequently be detected in vapors issuing from a clot of hot slag which is sprinkled or quenched with water. The formation of ammonia proceeds readily under a wide range of circumstances similar to those above, all of which point toward an external source of the gaseous elements involved.

L. F. REINARTZ, Middletown, Ohio.—Mr. Carl Peirce has presented a valuable paper on a subject that has been very widely discussed in recent years, especially since the demand for high finish, deep drawing and other grades of sheet steel in the lower carbon ranges has become an important factor in the steel business. Steel of this analysis has been produced for many years, but the product for which it was made did not require the extra care in the steel plant that it does today. It must now be worked down into thin sheets for special purposes and undergo many severe finishing processes both in the steel mill and in the fabricating plants. Mr. Peirce's paper has outlined in a concise and logical manner

the steps which must be taken in manufacturing such steels. The secret of success is attention to details of well known steel practices.

I agree with him that quality steels of this class cannot normally be made out of inferior raw materials. Scrap should be clean and if possible not too variable in analysis. Galvanized scrap or babbit are particularly objectionable. Scrap should be in such physical condition that undue delays are not encountered in charging the furnace. Limestone should preferably contain over 95 per cent. available calcium carbonate, and be free from clay or other foreign substances. Almost universal practice shows that 10 per cent. limestone is required for proper slag volumes to protect the metal from overoxidation. The use of 8 per cent. limestone makes the operation less fool-proof.

The pig iron, used as hot metal or cold pig iron, should not average more than 50 per cent. of the metallic charge. This pig iron should be about 0.90 to 1.10 per cent. in silicon, 1.50 to 2.00 per cent. manganese, and should show a clean, gray fracture with a high graphitic carbon as indicated by the break. If the silicon in the pig iron for any given charge is too high, the metal will not attain a proper action in the furnace at tapping time and "riser" steel is apt to result.

If the silicon in the pig iron is too low, due to blast furnace trouble, blisters and laminations are apt to occur in the sheets no matter how carefully the steel maker has worked his heat. This type of pig iron often does not allow the bath to hold the carbon and the heat melts "soft" with the attendant troubles, as Mr. Peirce has stated.

Melting practice undoubtedly has a very marked bearing on the quality of the finished heat. Mr. Peirce's scheme for checking up on the heats worked by various first helpers is worth while following up in other plants. It may account for the fact that a melter may produce good heats on one furnace and bad ones in another.

Spar, as every one will probably agree, must be used with utmost care, but every steel-plant man, if he is honest, will also agree that furnace men do not always follow the practices as set down by the superintendent of the department. This practice must constantly be watched. If a heat melts from 0.40 to 0.60 per cent. carbon, it is possible to work sufficient ore through the bath to get the heat in good tapping condition. Here again theory and practice must constantly be checked. The superintendent knows that best results will be obtained if oreing is discontinued from 0.10 to 0.15 points above the desired carbon and then rod the heat down. He must be constantly on the alert to organize the will of his furnace men so that they will carry out his instructions. I agree with Mr. Peirce that it is better to melt too high than too low. The more closely these two operations can be controlled the less off-grade heats will result.

Experience over many years has shown that in our practice, ore should be at least fist size, or larger, for best results in making rimming

steel. Smaller ore floats around in the slag and does not do its work as thoroughly as the heavier ore pieces.

We will all agree with Mr. Peirce that heats should not be worked down too hot in order that excessive gas volumes are not absorbed by the steel before it reaches the finishing stage. Such heats are apt to have high-iron oxide in the final slag, and require large doses of deoxidizer in the ladle and the molds to make the heat "set" properly. If the melter hits the right combination, he may produce a good heat, but the chances are against it.

Rimming steel containing 0.08 per cent. carbon and 0.30 per cent. manganese will undoubtedly rim better than a metal with a higher carbon or manganese. Such steel, however, is very apt to produce sheets that will have higher lamination and blister losses because the carbon in the bath has been driven lower and the bath contains more gases. An analysis of 0.10 to 0.11 per cent. carbon and 0.40 to 0.45 per cent. manganese will usually give better surface and internal conditions.

The addition of pig iron in a bath preliminary to tapping has been a more or less universal method for cleaning up the bath. However, there again, a great deal depends on the judgment of the melter as to the length of time to leave the pig iron in the bath and the amount to use. The same amount and the same length of time will not suit every condition. If not properly regulated, it may cause more harm than good, chiefly blisters or laminations. Usually if a heat has been rodded down properly and slag is in a mediumly active stage of boil, the addition of the ferromanganese in the furnace instead of in the ladle will clean the bath of oxides.

Care should be taken so that tap holes are not too large. The mixing of a "soft" steel slag and the metal before the ladle is more than two-thirds full is poor practice and causes bad steel.

Molds must be kept scrupulously clean. Iron oxide allowed to remain around the top of molds is bound to fall down on the stool, and cause trouble when the steel is poured into the mold. Sand or other siliceous material, used around the bottoms of molds to prevent fins must not get under the mold where the metal will strike it.

Rimming steel poured into very hot molds shortens the life of the molds. Such practice causes poor surface on the sheet bars made from the ingots poured into such molds. Damp molds cause blister troubles. Molds ordinarily should be about "hand warm."

I do not agree entirely with Mr. Peirce that small nozzles will always improve quality. The ordinary melter is primarily interested in getting his heat into molds. The more he is sold on the quality idea, the more chance he will take on the "cold" side when tapping his heat. However, the tendency will always be to tap a little hotter if he must pour his 100-ton heat through a $1\frac{1}{4}$ or $1\frac{1}{2}$ -in. nozzle. If, on the other hand, he

taps his heat at the proper temperature for producing a small rim, or plate skull, and then has his steel pourer teem the heat carefully through a 1 $\frac{3}{4}$ or 2-in. nozzle, better average results over a month's period will result.

Steel poured hot into molds will give clean pouring practice, but may cause "riser" steel and poor surface sheet bars.

Steel poured "cold," *i. e.*, with a 5000-pound skull, or larger, invariably causes dripping or running stoppers, and often requires the use of oxygen. Sides of molds are sprayed and on the average more scabs and blisters will result from this practice than from any other.

Practice differs with reference to the use of deoxidizers in the molds. The practice successfully followed in a number of plants is not to guess at the proper amount to add to the ladle, but deliberately to add such an amount that ordinarily will not quite take care of all the deoxidation; then by judicious use of small quantities of deoxidizers in the molds, to balance the variations in melting practice.

Mr. Peirce speaks of the formation of blowholes due to high temperature causing the bath to absorb iron oxide, and that when the temperature is decreased the carbon reacts with this oxide and forms carbon monoxide. I think we can probably all subscribe to this theory. I am rather inclined to disagree with the statement that this carbon monoxide sets free hydrogen and nitrogen which cause the blowholes. My own belief is that the carbon monoxide itself causes most of these holes.

Experiments have shown that in a rimming steel, the long horizontal lenticular blowholes found in the lower third of an ingot are formed within the first 4 min. after a 5000-pound ingot is poured. Ingots have been dumped when the skin of the ingot has solidified to a depth of about 2 in., or where normally the vertical line of spherical blowholes commences to form. The shell was then split. All the horizontal blowholes had already been formed in the lower part of the ingot as shown by the split ingot.

The action of the metal in the mold during the first minute after teeming determines what kind of an ingot will be formed. Very hot molds will not allow the metal to solidify and thus prevent the churning action due to the evolution of large bubbles of gases caused by the decreasing solubility of the gases in the metal. These gases cling to the mold walls and, unless the action is violent, they do not escape. The same result is obtained if the heat is too hot, or if some excess of deoxidizer holds back this strong boiling action. I would like more proof that these blowholes are due entirely to hydrogen. Miller in the 1914 Carnegie Memoirs says that the first gas given off from several rimming ingots was composed of 40 per cent. CO and 38 per cent. H. Just before solidification CO values were 25 per cent. and H 60 per cent. This would indicate greater hydrogen removal at the end of the freezing than at the beginning. As the action is most violent then, this might lend

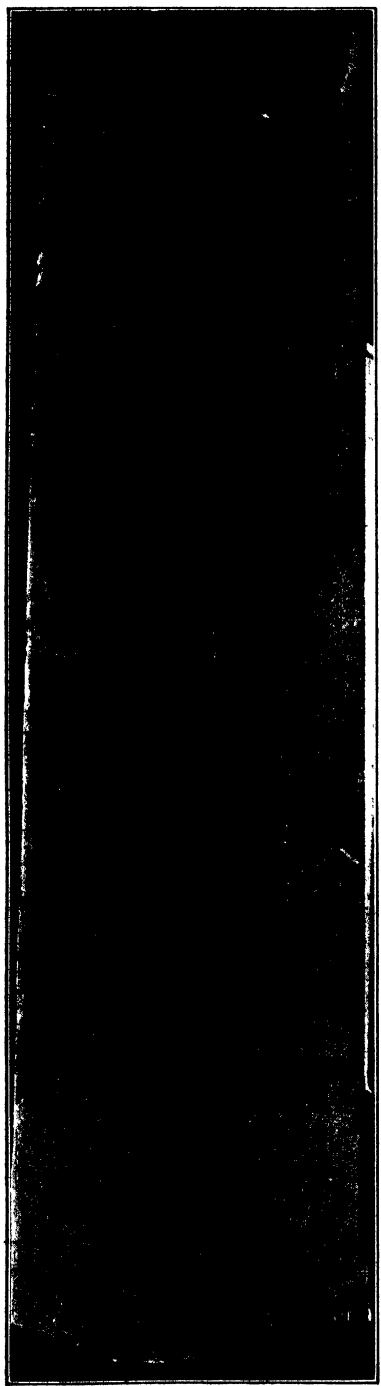


FIG. 4.—A SLAB SECTION SAWED FROM THE CENTER OF A 5000-LB. INGOT OF IRON IN WHICH THE ABSENCE OF SURFACE BUBBLES IS CLEARLY SHOWN.

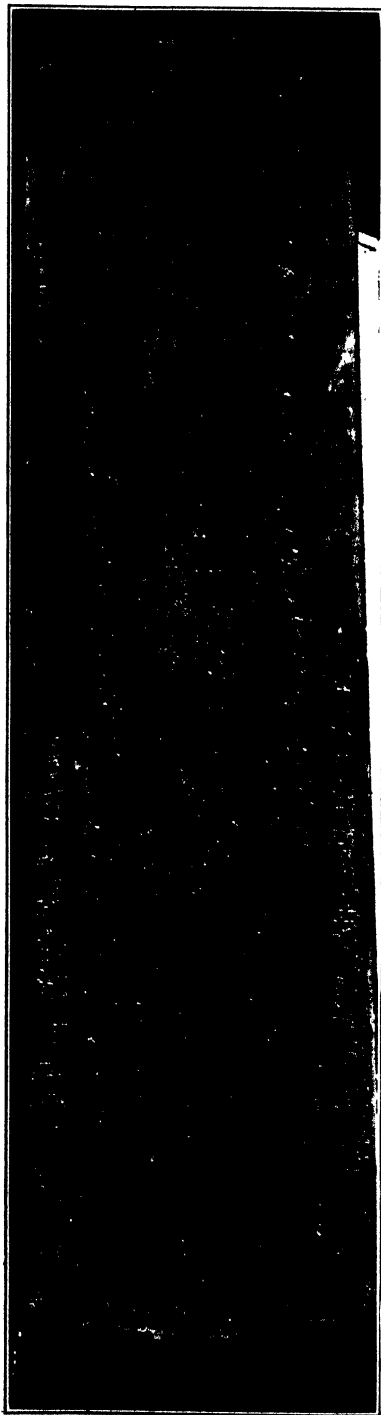


FIG. 5.—A SPLIT INGOT SHOWING A CONSIDERABLE NUMBER OF LENTICULAR SURFACE BLOW HOLES EXTENDING FROM THE BOTTOM OF THE INGOT HALF WAY TO THE TOP.

some aid to those who say the lenticular blowholes are caused by hydrogen. Hydrogen, being a very light gas, might be supposed on the other hand to free itself first from the mold walls.

When extremely low-carbon iron such as ingot iron is made, these lenticular blowholes no longer exist because a decided gasification begins as soon as the ingot is poured and gases have no opportunity to cling to the walls. When the central section approaches the stage where the metal becomes semi-pasty, a thin line of central vertical blowholes is formed (Fig. 4).

In making rimming steel only enough deoxidizer should be added to eliminate the free oxides in the bath, but not enough to increase the gas-holding power of the metal.

Fig. 5 shows a split ingot with a considerable number of lenticular surface blowholes extending from the bottom of the ingot half way to the top. Even if such an ingot is very carefully heated in the soaking pits, a large number of seams will be produced in the resulting sheet bars, causing serious rejections. Ordinarily the internal blowholes, if they are bright, as these were, will weld up. This type of ingot was produced by slightly overdosing the heat with aluminum, causing the metal to rise in the molds about 3 in. while rimming in.

The late Professor Crabtree of Carnegie always maintained that the best rimming steel should go into the mold with very little free oxide in solution. The strong releasing of carbon monoxide gases, so necessary in this process, should result from the metal losing its solvent power for gases, and not from carbon monoxide formed by an iron oxide-carbon reaction. The latter shows careless, dirty practice, which melters often try to cover up by heavy doses of deoxidizer in the molds.

Paul Klinger, in the January, 1925, issue of the Krupp monthly, has shown some interesting tests made on live, semi-killed and killed steels. His test proved that when live steels are poured into molds the first gas consists mostly of carbon monoxide. Later more hydrogen and carbon dioxide is evolved as the freezing progresses. In semi-killed steels, or those containing about 0.05 per cent. silicon, he showed that the gas evolved consisted of $\frac{1}{2}$ carbon monoxide and $\frac{1}{2}$ hydrogen. In killed steels containing about 0.15 per cent. silicon, or more, the volume of gas was very much less than for rimming steel, and this gas was for the most part hydrogen. He also showed that the length of time the heat was held in the ladle had no influence on the composition of a well made steel. He claimed that carbon monoxide cannot be kept in solution in freezing steel and that the carbon monoxide evolved from rimming steel was caused primarily by an iron-oxide-carbon reaction. This claim did not seem to be reasonable as Armco ingot iron containing no carbon, produces a very live evolution of carbon monoxide gas during teeming operations. A very gassy heat may be run from the furnace

into a ladle and the metal killed with silicon so that no gas is evolved during pouring operations. It stands to reason that this gas has gone into solution.

When rimming ingots are rolled, considerable gas is evolved which undoubtedly is carbon monoxide gas. In a soft-carbon rimming steel an excess of deoxidizer holds gas in solution and thus prevents rapid evolution of gas, which sweeps away the gas that causes surface blowholes. If carbon monoxide gas in rimming steel would be caused primarily by reaction of carbon and iron oxide in the metal, the composition of the metal at the end of a pour would be much different than at the beginning of a pour.

We know that when a heat has been overoxidized in a furnace that such action does take place, but the metal in the molds will be practically unfit for use and the carbon and manganese in the last part of the heat will be much lower than in the balance of the heat.

Whatever method is followed, it cannot be considered a cure-all. Practices in one plant cannot be transferred bag and baggage to another shop, as almost every steel-plant man has found to his grief at some time or another. Each individual must start out with the generally accepted correct principles and then work out the detail practices to suit his own conditions.

H. D. HIBBARD, Plainfield, N. J.—I cannot give all the evidence as to what gases form these various holes. Some 15 or 20 years ago I came to the conclusions that are set forth in the paper. They were based to a considerable extent on the available gas analyses, which were a most discordant lot and were taken under different conditions. Nevertheless, the classification seemed to apply, although I have never presented it as a definite proposition.

I have always qualified my statement that hydrogen probably was the chief ingredient of the skin holes, carbonic oxide the next, and nitrogen and ammonia next. In regard to nitrogen and ammonia I have some evidence; I have smelled the latter issuing from the center of the ingot and from the pipe cavities and split rail ingots. These also gave an alkaline reaction. So I think that until disproved by analyses, I can continue to abide, tentatively, by my conclusions.

Mr. Reinartz, has gone into that so fully that I might mention a little thing that happened about 10 years ago when I was at their plant at Middletown; I was talking to Mr. Aupperle about these gases. I had been trying to get people in the steel works to do some research work to find out what those gases were, and I went through it with him. I pointed out the various holes, and I said, "Manifestly they are made by different gases." He was very much interested indeed. He said he believed he would try it, so I sketched out a way in which he could mount a specimen under a radial drill, drilling to 45° under a mercury bath, and collect his

gases and analyze them. It has never been done, I think. Drilling over water is of no use because of the hydrogen reaction with the fine particles of iron.

We went out into the laboratory and found that they had tucked away ample apparatus for making the whole test. It was not being used but it was there. It cost hundreds of dollars, I guess. He was quite taken with it and said in 6 months he would let me know what he had done. In 6 to 8 months, I wrote asking him what he had done, and he had done nothing. Since then they have done nothing; I have been assured of that at this meeting.

If any of you want to take this up, there is a great field for research, because if we knew what those gases were, we certainly would be able to deal better with them than by guessing.

Mr. Peirce quotes me as having made statements, but he does not give the qualifications. As I say, I have always endeavored when I made these statements, to qualify them by saying that to the best of my knowledge and belief it was so, but I cannot prove it.

This last split ingot he shows is an extraordinarily fine one, only he does not give the analysis. If it was ingot iron, it would not be anything extraordinary; but if it was 12 carbon steel, it would be very fine. I was in hopes he would be here, and I would like to know something about the furnace practice that produced that ingot.

Speaking of the paper in general, we see so many statements that a steel was good or a steel was bad, but that does not tell very much. If we could be told in what way it was good and in what way bad, that would help us to understand the paper much more satisfactorily.

I did mark one thing, and that is on page 1035 where he speaks of the minimum number of hydrogen blowholes in the lower third of the ingot. They ought not to be up so high as a third. A good ingot of 12 carbon steel, I claim, ought not to have the blowholes on the side more than 10 per cent. of its height anyway. It ought to be from 5 to 10 per cent. I think that a third is too much, and I imagine that if he undertook to make sheet bar of that, he would find that he would have some split sheets resulting from those holes down there.

I want to reserve the right Mr. Chairman, to send in some written discussion after I have had the time to read the paper carefully.

J. V. W. REYNDERS, New York, N. Y.—I hope you do so, at the same time carrying the subject forward to a point that will reduce the qualifications to a minimum.

C. L. KINNEY, Jr., Chicago, Ill.—I have heard it stated that in the making of rimmed steel it is very necessary to work with a little residual manganese. I note that Mr. Reinartz says that in their pig iron charge the manganese ran from 1.50 to 2 per cent. I would like to ask Mr.

Reinartz what his residual manganese may be in that particular type of steel made with that particular type of iron?

L. F. REINARTZ.—0.15 to 0.18.

C. L. KINNEY, Jr.—Would you consider that working with one ranging from 0.25 to 0.30 it would be impossible to make rimmed steel?

L. F. REINARTZ.—I would rather not work over 0.20.

C. L. KINNEY, Jr.—In making steel for other types of work, say other than sheet bars or plate steel, for example, ranging in carbon from 0.15 to 0.25, would you prefer to work with a lower residual manganese or work with a higher residual manganese and perhaps get better physical properties in your steel?

L. F. REINARTZ.—From my experience, I believe I would rather have a low-manganese iron for plate steel. You get a more live reaction.

C. L. KINNEY, Jr.—Would you anticipate that generally speaking you would get better physical results, we will say, in your physical laboratories, with a 0.15 residual manganese as opposed to a 0.25 or 0.30?

L. F. REINARTZ.—I do not know. I have never gone as high as 0.30.

C. L. KINNEY, Jr.—I am particularly interested in the manufacture of plate steel, and one of our difficulties is the production of a good surface. We feel that working with a high-manganese iron and with a high residual manganese that we have gained a great deal so far as the physical characteristics of the steel are concerned. On the other hand, we do have a great deal of trouble with the surface imperfections, most of which seem to take the form of what we call a blister or a scab. I am very certain, from ingots which we have split, that our blowholes are not where they should be. It is merely a question now of our trying to eat our cake and have it, too; that is, whether or not we sacrifice something in the way of a physical quality by going down, let us say, to a 0.10 residual manganese and gaining something in the way of surface.

A. H. WOODWARD, Woodward, Ala.—I might answer Mr. Kinney's question on residual manganese. I think Mr. Peirce attributed his success in rimmed steel to a high residual manganese. He brought that out at the meeting in Cleveland last October, and every one was interested in how he maintained a high residual in rimmed steel, which I hope to have him tell us at Chicago in April. I think he runs his residual somewhere around 0.20 or 0.25.

C. L. KINNEY, Jr.—It is not at all difficult to maintain a 0.20 or 0.25 carbon, provided your slag is all right.

V. B. BUCK, New York, N. Y.—I can bear out Mr. Kinney's experience with surface defects with high residual manganese. We have been running some experiments along that line both on sheet bar and on plate work, and there is a tendency for a much poorer surface in the plate. We do get

increased physical properties much easier in the physical laboratory; it is much easier in the physical laboratory to get by; but in the end, for the surface, which a great deal of our work demands, high residual manganese is detrimental.

A. L. FEILD, Long Island City, N. Y.—In connection with Mr. Hibbard's statement regarding hydrogen and the formation of blowholes, I believe that most of the conclusions regarding hydrogen have been drawn from gas samples taken from the gas issuing from the rimming in steel or from the solidifying steel. I happen to know, however, that recent developments in analytical methods for total oxygen and hydrogen in the finished steel seem to show that the more refined the method of analysis becomes, the lower the hydrogen content of the steel seems to be. In fact, it would appear that with precise methods, the average steel contains no hydrogen to speak of, that is, it is in the three ciphers on the right, probably around 0.0004 per cent.

That raises a question. Hydrogen as every one knows, diffuses very rapidly through iron, in fact, you can drive it off usually from solid iron at a low red heat. Therefore, do the solubility relations of hydrogen and steel ever suffer such a sudden change as to cause the actual liberation of hydrogen in the form of a blowhole? It would seem that hydrogen should escape from liquid steel just as water does from a sieve. The escaping tendency is so high that it never comes out in the form of a bubble. I think this should be determined experimentally.

In connection with the different types of blowholes, I expect it has been observed by every one who has split ingots, that the outside blowholes are very bright, unless they are too near the surface and are oxidized. They are like silver almost, showing that the cavity must either have contained a reducing gas or else must have contained a neutral gas. The blowholes in the center of the ingot, as you know, are not very apt to be so bright.

One interesting point in connection with the surface of the lenticular blowholes that I have observed and which probably others have observed, too, is that they are practically always corrugated, as though they were a long ellipse which had been corrugated. They are definitely scalloped at the borders. I have often wondered what caused the peculiar surface formation of those blowholes. It must be connected with their mode of formation during solidification.

Professor Hibbard's statement that ammonia is probably one of the gases is very interesting, but I believe that ammonia is decomposed by iron at a fairly low temperature, and that you would get iron nitrite or dissolved nitrogen and hydrogen if ammonia were present.

L. F. REINARTZ.—I would like to bear out Mr. Hibbard's statement; we have smelled ammonia gas in steel. However, it was in killed steel. We have never experienced the ammonia in any rimming steel.

Another thing that I did not bring out in regard to the formation of those blowholes, is the fact that the formation of those on the surface depends largely on the action of the metal. If there is very little action of the metal right when you begin to solidify, you are going to have a considerable number of lenticular blowholes, that can be produced mechanically as well as by the metal.

If an ingot that will rim perfectly in one mold, say at ordinary temperature, is poured into a very hot mold, it will rise some 5 or 6 in. and will have a tremendous lot of blowholes. In other words, the hot mould has prevented the rapid reduction of temperature of the skin of the ingot and thus has allowed a certain amount of gases to collect in the lower part. I believe also that the temperature has much to do with the formation of those blowholes in the lower part of the ingot because you never find them in the upper part of the ingot. We have split ingots that were rather squatty that did show less blowholes than the longer ingots.

Another cause of those blowholes is a slight overdeoxidation of the metal. If you put just a little bit too much deoxidizer in your ladle, you are very apt to have a metal that will not allow the gases to be liberated immediately. This is due to the effect that the deoxidizer has in retarding the evolution of the gases by holding them in the solution until the temperature drops a little; then they are released from solution, and regular action, just like any other ingot follows. What happens at the beginning is what causes the trouble, and, as Mr. Kinney has said, the high residual manganese has a tendency to retard that action at the beginning of the evolution of the gases, and therefore, despite the fact that he has a cleaner steel, he has a steel which will have worse surface conditions because of the formation of those blowholes too close to the surface.

H. D. HIBBARD.—I would like to say another word. Mr Feild speaks about the weight of hydrogen. The weight of hydrogen to form those blowholes is so small that it could be detected only by volumetric analysis. Gravimetrically, it is zero. He objects to my saying that ammonia is in steel, because he thinks it ought not to be there and, therefore, it is not. But I know it is because I have smelled it.

J. V. W. REYNDERS.—I would like to remark that this paper and the very practical points brought out in the discussions constitute a valuable contribution to the steel making art. Probably no subject is of greater interest and importance just now to open-hearth men. I wish very much that it were possible to devote the whole session to it. I am going to suggest that the discussion be placed on the agenda for the Chicago Open Hearth Conference because we have not had the opportunity at this time to bring out many of the important phases connected with the manufacture of rimmed steel.

Combustion in the Open-hearth Furnace with Special Reference to Automatic Control

By K. HUESSENER,* PITTSBURGH, PA.

(New York Meeting, February, 1926)

IN presenting the following data on combustion in the open hearth furnace and the advisability of automatic combustion control, the author finds himself much more severely handicapped by the lack of reliable test results than he had anticipated when he first undertook to write this paper.

In order thoroughly to investigate how the results of an open-hearth furnace are influenced by combustion, one would have to draw up a large number of heat-balance sheets, as Kinney and McDermott¹ have given for one heat in their extremely able paper on "Open Hearth Efficiency," presented before the American Iron and Steel Institute on October 27th, 1922. Instead of covering only one heat, however, such heat-balance sheets would have to embrace a large number of heats, and not only for one kind of fuel, but for all the various fuels in customary use.

USE OF RADIATION-PROTECTED PYROMETER

Such tests necessitate extremely careful temperature readings, and here the first serious difficulty presents itself. Nearly all the temperature readings so far published have been taken with thermocouples for the lower ranges and with optical or radiation pyrometers for the higher ranges. This method of measuring reveals the temperature of the surrounding walls, or in the case of optical or radiation measurements, the temperature of that part of the opposing walls which has been focused by the instrument. The error in ascertaining the temperature of the gases entering or the waste gases leaving the checker chambers is probably not very large, as the flowing gases impart their temperature to the walls of the flues. On the other hand, the uptakes, where the preheat temperature of gas and air are usually measured, are under the influence of radiated heat from the port ends, and correct temperature readings can here be taken only by using a radiation-protected pyrometer of the aspirating type.

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¹ C. L. Kinney, Jr., and G. R. McDermott: The Thermal Efficiency and Heat Balance of an Open-hearth Furnace. Iron. and Steel Inst. *Year Book* (1922), 464.

In the course of the author's tests on a 100-ton open-hearth furnace, using producer gas as fuel and equipped with Steinbart automatic control, it became necessary to measure the temperatures obtained in preheating the air. An aspirating pyrometer was used, as shown in Fig. 1.² The stack draft was utilized to pull the gases out of the checker chambers. As the couple of the pyrometer was completely protected against radiation, the temperature of the gases themselves was measured. The use of this type of pyrometer is strongly recommended; or better still, the construction shown in Fig. 2. As a result of these measurements, the author was truly surprised to find that the preheating temperatures of the air, which were measured only in this instance, proved to be very much lower than had been anticipated. The average of over 100 readings extending over 6 hr. amounted to 1360° F., the lowest average during a reversal being 1280° F. and the highest 1450° F. It should be mentioned that these measurements were taken very shortly after rebuilding.

CALCULATIONS OF THE EFFECT OF DIFFERENT FUELS AND DIFFERENT AMOUNTS OF EXCESS AIR

A careful examination of the figures obtained did not reveal anything to indicate that they might not be correct. The author, therefore, decided to calculate theoretically what preheating temperature might be expected from a furnace of this type. The tables given in the appendix give a review of how the use of different fuels with different amounts of excess of air will influence the results from a 100-ton open-hearth furnace as it is at present usually built: Hearth surface, 580 sq. ft.; air-checker surface, 4175 sq. ft.; gas-checker surface, 2710 sq. ft.; or a relation between hearth surface to checker surface of 1:11.87.

Assumptions Made in Calculations

Before explaining the calculations and the conclusions drawn therefrom, it will be necessary to show why certain assumptions had to be made in order to be able to set up these tables. In view of the fact that the temperature at which the bath in an open-hearth furnace is active, is between 2800° and 2850° F. and further, in view of the fact that there must be a temperature drop if there is to be any heat transfer from the gases to the bath, we must assume that a minimum temperature of the gases of 3000° F. is necessary, if any work in the open-hearth furnace is to be done at all. The active heat in an open-hearth furnace can therefore only be that portion of the heat contained in the gases that carries the temperature beyond 3000° F.

As the gases must remain active until after they actually have left the hearth room and enter the ports, we must assume that at the point of

² All figures and tables are given at the end of the text.

leaving the hearth room, these gases still have a temperature of 3000° F., as otherwise, the outgoing end of the bath would always remain inactive, which, as is very well known, is certainly not the case. In following the course of the waste gases through the ports, uptakes and checker chambers to the reversing valve, we find a temperature drop from 3000° to about 1250° F. This exit temperature of the waste gases leaving the checker chambers of 1250° F., has also been assumed by the author to be a constant for the present type of furnace. The reason for this assumption is that in taking careful measurements, it was found that by doubling the flow of gas through an open-hearth furnace, the increase in exit temperatures was never more than 75° to 100° F. Therefore, for all practical purposes, it can be assumed that this temperature is actually fixed for the present type of checker chamber. The reason for this rather strange uniformity of exit temperatures is, in the author's opinion, to be found in the fact that today's type of check chambers does not by any means favor a uniform distribution either on the ingoing or on the outgoing end, so that large portions of the chambers are evidently always inactive. It appears that an increase in the quantity of gases reduces the inactive portions, and, conversely, a decrease of such quantity results in an increase of inactivity.

Accepting a fixed temperature of 3000° F. for the gases leaving the hearth and of 1250° F. for the gases leaving the checker chambers, we have a temperature drop of 1750° F. which must provide first, for the losses through radiation and conduction in the ports, uptakes and checkers, and, second, for the preheating heat of the air and the gas entering the checker chambers. In our calculations we encounter here the second difficulty which will probably lay us open to criticism, but, as certain assumptions will have to be made if the study of the combustion problems in an open-hearth furnace is to be carried any further, we believe that the method in which we provide for these losses will be at least approximately correct. In the paper by Kinney and McDermott³ the temperature of the gases entering the checker chamber from the uptakes is given at approximately 2300° F. For the purpose of our calculation, we have accepted this figure as being approximately correct, and, therefore assume that all the losses, except the stack losses, are covered by the temperature drop from 3000° to 2300° F. That no serious error has been committed by this assumption, is, as will be seen later, evidenced by the fact that the calculated possible preheating temperatures approximate very fairly those ascertained by actual measurement. Another assumption which we had to make in order not to complicate matters too much, is that complete combustion of all the gases is always obtained before they leave the hearth. In other words, in our calculation we do not take

³ C. L. Kinney and G. R. McDermott: *Op. cit.*

care of any losses that might be due to portions of the gases not being completely burned over the hearth.

The author feels justified in assuming such complete combustion, as it has been found that with automatic combustion control such losses are almost entirely eliminated. It is, of course, a fact that to burn all the CO gases generated by the reactions of the bath is often impossible because the necessary time to complete combustion is lacking before these gases reach the ports. The author believes that he has almost completely covered this source of error by crediting the process heat with the full amount of combustion heat derived from these gases in the form of exothermic heat. What actually happens is that these gases burn in the checker chambers, resulting in a consequent increase of the preheat temperature, and after all, the bulk of the heat thus lost is subsequently carried back to the bath.

As explained above, we have found that the exit temperature of any given checker chamber is not materially influenced by the quantity of waste gases passing through it. For this reason, it should be permissible to assume the same exit temperatures for all kinds of fuels. As a matter of fact, the author knows that for the 100-ton furnace under review, there are no worth-while differences irrespective of whether the furnace is operated on straight coke-oven gas, tar, oil or producer gas.

Discussion of Tables 1 to 6

In connection with the calculations, which are given in the Tables, it must be kept in mind that the sole purpose is to furnish comparatively correct figures. We believe that even if mistakes in our assumptions should have been made, these would materially change only the actual results obtained but not the relations between the results for the different fuels and for the different amounts of excess air.

Table 1 shows the weight of the combustion air, the weight of the products of combustion and the heat content of these products of combustion at 3000° F. for different amounts of excess air from 0 to 40 per cent. These figures are interesting from several points of view. First of all, they show the tremendous weights of gases handled in the average 100-ton open-hearth furnace. Assuming that such a furnace makes 10 tons of steel per hour with a heat consumption of 6,000,000 B. t. u. latent heat, per ton of steel, and that the gas is completely burned with an excess of air of 30 per cent., then the weight of the gases passing through the furnace on an average hour, is in excess of 60,000 lb. This will explain better than anything else the mechanical wear on the furnace ports and roof, which must eventually be worn down even if no damage by heat would be done to them at any time.

The heat content at 3000° F., given in Table 1, is the amount of heat that is available for providing for all radiation and conduction losses in

the outgoing port, down-takes, checkers, and stack, the remainder being the amount of heat that will be carried back into the furnace as preheat of gas or air on the next reversal period. Table 1 shows that a temperature of 3000° F. cannot be obtained without preheating when using producer gas, whereas it is obtainable with natural gas and oil.

Table 2 shows how the heat content in the gases with different amounts of excess air is reduced by a temperature drop from 3000° to 2300° F. and from 2300° to 1250° F. As explained above, the drop from 3000° to 2300° F. given for each gas, for instance in columns 2 and 3, is assumed to take care of all the losses due to radiation and conduction, at the outgoing end of the furnace. The differences between the heat content in the 2300° F. columns and the 1250° F. columns, are the amounts of heat carried back into the furnace. This is all the heat actually available for preheating both gas and air.

Table 3 tabulates these amounts, which have been obtained by deducting the figures in the 1250° F. columns from the figures in the 2300° F. columns in Table 2.

Table 4a gives the heat available in the products of combustion above 3000° F. resulting from the latent heat of the fuel and the heat absorbed by the combustion air during preheating. The figures refer to natural gas, coke-oven gas and oil with different amounts of excess air from 0 to 40 per cent., for preheat temperatures from 32° to 2200° F. Taking into consideration the amounts of heat in the waste gases actually available for preheating, as given in Table 3, we find the values of B. t. u. available above 3000° F. as entered between the lines of Tables 4a, 4b, and 4c and have marked same by running a line crosswise through the table, adding below the corresponding temperatures of preheat obtainable. We find that these temperatures do not materially vary, no matter whether the gas is burned with, or without an excess of air up to 40 per cent. As these possible preheat temperatures are still above the temperatures which we ascertained by actual measurements the conclusion is permitted that even by allowing a temperature drop from 3000° to 2300° F., all the losses between the port end and the reversing valves have not yet been properly covered. By increasing this allowance for losses, the possible preheat temperatures given in Table 4a would be reduced, but even then there would not be any change for the different amounts of excess air. The calculations so far appear to show that with coke-oven gas, natural gas and oil, when air alone is preheated and when the present customary type of open-hearth furnace is used, no higher preheat temperature than 1450° F. can reasonably be expected.

In Tables 4b and 4c, the same calculations are carried out for producer gas containing 150.3 and 132.5 B. t. u. (columns 5 and 6, Table 3.) In these two tables matters are a little complicated, as

both gas and air are preheated. Our temperature measurements, previously mentioned, were taken on such a furnace and it is, therefore, fairly safe to assume that a preheating temperature for air of about 1500° F. with a preheating temperature for gas of 1600° F. will usually be found in open-hearth furnaces of this type. If the preheating temperatures for air should be higher, the preheating temperature for gas would be lower, or vice versa. In either case the operation of the furnace would not be affected as the total amount of heat carried back into the hearth as preheat always remains the same.

Attention is next turned to the hearth itself to compare the amounts of heat which are here available for the process of making steel, and which at the same time provide for the unavoidable losses through radiation, conduction and cooling water. These amounts of heat are shown in Tables 4a, 4b and 4c in the figures above the line drawn crosswise through these tables. Here we find for the first time how seriously an open-hearth furnace is affected by the excess of air with which the fuel is burned. Thus under the column of natural gas in Table 4a, the available heat that stays in the bath is 511,000 B. t. u. for every million B. t. u. of latent heat admitted, if the gas is burned with no excess of air at all. This available amount drops to 349,000 B. t. u. with an excess of air of 40 per cent. The comparative figures for coke-oven gas are 519,000 reduced to 369,000 B. t. u., and for oil 565,000 reduced to 413,000 B. t. u. It is surprising to find that the two kinds of producer gas, as fuel, appear to be superior to natural gas and coke-oven gas and only slightly inferior to crude oil.

These figures of available heat in the hearth now put us in a position to calculate the heat consumption per ton of steel, assuming a certain duration of a heat. The available heat, as has already been stated above, has to cover, in addition to the process heat proper, the radiation, conduction, and cooling water losses. As we have no reliable figures regarding these losses for the 100-ton open-hearth furnace under review, we have accepted the figure given by Kinney and McDermott. In accordance with the balance sheet given in their paper, the losses of an 80-ton open-hearth furnace amounted to 88.1 million B. t. u. for a duration of heat of 9 hr., or 9.8 million B. t. u. per hour, which covers the radiation and cooling-water losses of the outgoing port. As we in the present instance are examining in a 100-ton furnace the heat conditions of the hearth only and not including the outgoing port, we have assumed that this figure of 9.8 million B. t. u. lost per hour will be about correct for the larger furnace. Even if this were not so, it would only influence the actual figures which we hereafter calculate, but not their relative sizes. With regard to the process heat, we have also accepted the Kinney and McDermott figure of 1,060,000 B. t. u. per gross ton of steel made.

If we assume that 100 tons of steel are to be produced in 12 hr., then the process heat required for 100 tons of steel will be 106 million B. t. u. The radiation, conduction, and cooling-water losses will be 12×9.8 million B. t. u., or approximately 118 million B. t. u. In other words, for every ton of steel produced, 2,240,000 B. t. u. must enter the bath and supply the radiation, conduction, and cooling-water losses. By referring to Table 4a, we find that for natural gas burned with no excess of air, the available heat in the hearth is 511,000 B. t. u. for every million B. t. u. of latent heat admitted, so that it will take $\frac{2,240,000 \text{ B. t. u.}}{.511} = 4.4$ millions

B. t. u. latent heat in the fuel in order to make one ton of steel, provided that it takes 12 hr. to finish the heat. If the heat is finished in 10 instead of 12 hr., the process heat will still have remained 106 millions B. t. u. but the radiation, conduction, and cooling-water losses will be cut down to 10×9.8 millions B. t. u. = 98 millions B. t. u., so that the total heat requirements per ton of steel would only have been 2.04 millions B. t. u. The same amount of 511,000 B. t. u. being available in the hearth, it will be possible to make one ton of steel with $\frac{2.04}{.511} = 4$ millions B. t. u.

latent heat. In exactly the same manner the required amounts of latent heat for excesses of air from 0 to 40 per cent. have been calculated, and for durations of heat of 12, 10, and 8 hr. for the five kinds of fuels (Table 5).

Looking over these figures, we find that crude oil is approximately the best kind of fuel, by 10 per cent. Natural gas shows the greatest drop in efficiency with increased excess of air, whereas producer gas is about equal to coke-oven gas. It is very interesting to note how very little the results are influenced by the quality of the producer gas, but one must not forget that after all the gas with 150 B. t. u. means a considerably larger producer efficiency than the gas of 132 B. t. u. and will, therefore, reduce the pounds of coal per ton of steel. The figures given in Table 5 for producer gas are in millions B. t. u. latent heat in the gas and not in the coal. The gas of 150.3 B. t. u. would correspond to a producer efficiency (latent heat in gas: latent heat in coal) of 79 per cent., and the gas of 132.5 B. t. u. to an efficiency of 72 per cent. We have entered in brackets, under these figures of required latent heat in the gas, the pounds of coal of 13,500 B. t. u. per ton of steel at these producer efficiencies. In the same way, we have entered the amounts of fuel required for natural gas, coke-oven gas and oil.

Table 6 shows the average flow of fuel per hour necessary to obtain the results given in Table 5, assuming that the fuel could be admitted to the furnace in uniform quantities every hour. Actually, of course, the flow during the melting period is very much larger than during the refining period. This table shows very clearly that to get good fuel economy in an open-hearth furnace, two things are absolutely essential:

One is to regulate combustion by keeping the excess of air as near as possible to zero; the other is to burn as much fuel as possible in a given time. A comparison of Tables 5 and 6 shows that by increasing the flow of natural gas from an average of 36,000 cu. ft. per hour to an average of 44,400 per hour (always provided that all the gas is being completely burned before it leaves the hearth, and with no excess of air), we reduce the time of the heat from 12 to 8 hr. (Table 6), and the heat consumption from 4.4 millions to 3.6 millions B. t. u., latent heat per ton of steel (Table 5). The need for burning increased quantities of gas per hour demands the installation of forced-draft fans capable of supplying enough combustion air at all times and of induced-draft fans where the available chimney draft is not enough to handle the increased quantities of products of combustion. In this latter respect, changes will usually not be necessary; if the excess of air is cut down, the amount of waste gas, even from larger consumption of gas, will usually not be larger. For instance, Table 6 shows that by cutting the excess of air down from 20 to 10 per cent., for a furnace using natural gas, the same rate of flow of gas will result in reducing the duration of a heat by 2 hr. and the fuel consumption from 5150 to 4240 cu. ft. of gas per ton of steel. The same condition holds for coke-oven gas.

It would be hasty to conclude that fuels can be positively compared to each other on the strength of Tables 5 and 6, because of the difficulty of obtaining complete combustion. Table 5 shows that with an excess of air of 40 per cent. in a 12-hr. duration of heat, only 38.5 gal. of oil should be used per ton of steel, and with the same excess of air for an 8-hr. heat, this consumption would only be 31.6 gal. There are, without any doubt, many furnaces that will complete 100-ton heats on oil in 8 hr., but their fuel consumption will usually be above 36 gal. per ton of steel and often even considerably more. The reason, in the author's opinion, lies in the difficulty of obtaining complete combustion of the oil. It is extremely hard, if not impossible, to atomize the oil properly with the combustion arrangement as used at present. With producer gas, the difficulty in obtaining the results as shown in Table 5 lies probably in the very large quantities of gas which have to be handled, and in the fact that the checker chambers are quickly sooted up, so that even if enough air can be forced into the furnace for combustion, there is always a certain amount of difficulty with the draft. Besides, it should be mentioned here, all our figures have been based on dry producer gas, which in actual practice is, of course, not available. The moisture in the gas will naturally reduce the temperatures obtainable over the hearth and, therefore, the heat available above 3000° is in practice smaller than the figures shown in Tables 4b and 4c.

The results for coke-oven gas in Table 5 have actually been obtained for a considerable period by the help of automatically controlled combus-

tion. This fact alone would tend to show that the calculations submitted in this paper are, to a certain extent, borne out by facts. The author's experience with natural gas is not sufficient, so far, to allow him to venture any opinion, although there does not appear to be any reason why the figures calculated in Table 5 should not at least be approached.

OPERATION OF A FURNACE WITH COMBUSTION CONTROL

One of the purposes of combustion control is to make the furnace independent of the chimney effect of the checker chambers for the supply of air. For this purpose, an induced-draft fan is installed usually in the passage between the two regenerator chambers as shown in Fig. 3. The air is taken into the fan through an intake box carrying an orifice plate. The quantity of air entering the fan is thus measured by the draft set up in this intake box, which represents the drop from atmospheric pressure through the orifice. From the fan, the air is conveyed to an auxiliary air-reversing valve, which consists of a steel-plate box equipped with cast-iron mush-room valves. These latter are tied in with the operating mechanism of the main reversing valve, so that their reversals are automatic, together with the reversals of the furnace.

Fig. 3 shows an open-hearth furnace which is equipped for coke-oven or natural and producer gas. If the furnace is fired with either coke-oven or natural gas, the quantity of gas is measured by an orifice plate in the main gas-supply pipe ahead of the reversing valves. For the purpose of having the quantity of air that enters the regenerators automatically follow the quantities of gas passing through the orifice plate, a Huessener combustion regulator is used (Fig. 5).

This combustion regulator consists of two pairs of concentric double bells. As gas pressures often in excess of 5 lb. are used, the smaller interior bells, which receive the differential pressures from the gas-orifice plate, are sealed in mercury. The air pressures, which only range up to 7 in. are taken care of by an oil seal for the larger exterior bells, which are piped up to the air-intake box and the atmosphere respectively.

The principle of the regulation is as follows: If the differential pressure set up by the gas-orifice plate is represented by the equation $G1 - G2$, in which $G1$ is the higher and $G2$ the lower gas pressure, and in the same manner, the differential pressure set up by the air-orifice plate by $A1 - A2$, in which $A1$ is the higher air pressure (in this instance atmospheric) and $A2$ the lower air pressure; and if further, the ratio between gas and air pressure which it is desired to maintain at all times is $1 : z$; then the regulation would be represented by the following equation—

$$\begin{aligned} G1 - G2 &= z(A1 - A2) \text{ or} \\ G1 + z.A2 &= z.A1 + G2 \end{aligned}$$

The action of the regulator follows this second equation. The double bells on one side of the beam receive the higher gas pressure and the lower air pressure, and the pair on the other side the higher air and the lower gas pressure. The ratio $1:z$ is being taken care of by making it the relation between the areas of the gas and of the air bells.

The bells are carried by a common beam supported by a fulcrum. The motive power of the regulator is a compressed air cylinder, the pilot valve of which is geared to the above mentioned beam. The piston rod of the motor is connected to a butterfly valve arranged in the combustion-air supply main. If the gas flow to the furnace increases, the difference $G1 - G2$ becomes larger, with the result that the pair of bells that receive the higher gas pressure will move up, compressed air will be admitted through the pilot valve to one side of the piston that moves to open the air butterfly-valve, until the equilibrium between $G1 - G2$ and $z \times (A1 - A2)$ is restored, when the regulation stops. Assume, for instance, that the furnace is operated on coke-oven gas and is passing gas at the rate of 150,000 cu. ft. per hr. and air at the rate of 750,000 cu. ft. per hour, and that, the charge having been melted down, the gas has to be reduced to 80,000 cu. ft. per hour; then the amount of combustion air admitted will immediately and automatically be reduced to 400,000 cu. ft. per hour, thus still holding the same relation of one volume of gas to five volumes of air.

If it is desired to change the character of the flame during the operation of the furnace, the relation between gas and air can immediately be changed by changing the size of the air-orifice plate on the air-intake box. This can be done by inserting a second smaller orifice plate in a frame which from the operating floor can be immediately lowered over the larger air-orifice plate. The connection between the reversing valve and the air regenerators is usually made underground (Fig. 4). The portion of the combustion air, that is to be sent into the gas regenerators, is either sent to the producer gas main, not in use, if the furnace is equipped for such gas, or into the air-inlet openings.

Regulation of a producer-gas furnace is difficult because hot producer gas cannot be reliably measured. For this reason, the regulation for producer-gas furnaces follows the principle that the air supplied to the producers is measured and that the combustion-air flow is automatically kept in strict relation to the producer air-flow. In order to equip for regulation an open hearth fired with producer gas, a blower to supply air to the producers must be installed. Preferably, this blower should be driven by a steam turbine of such size that the exhaust steam is just enough to supply the steam needed by the producers. Figs. 3 and 4 show diagrammatically such an installation for a three-producer plant. The producer blower is also of the single-inlet type equipped with an air-intake box and an orifice plate, so that the suction in the intake box, being

the drop from atmospheric pressure, is a measure of the rate of flow of primary air into the producers and, thus, of the amount of gas generated. The other equipment for regulation is the same as that described for coke-oven and natural gas, except that the type of regulator used is the one shown in Fig. 6. This regulator consists of two single bells carried by a common beam and fulcrum. One bell is connected to the air-intake box of the combustion-air fan and the other to the air-intake box of the producer fan. The two orifices carried by the two intake boxes are of such size that at equal suction the desired relation between producer air and combustion air is automatically upheld.

A furnace so equipped is operated by the heater on the floor, who is in control of the steam valve governing the supply of steam to the turbine of the producer air-blower. By opening and closing this valve, he will absolutely control the quantity of gas admitted to the furnace. This furnace becomes a one-valve control furnace. By admitting more steam to the blower, more air is sent into the producers, more gas is produced and sent to the furnace, and automatically the right proportion of additional air is admitted to the furnace by the combustion regulator automatically opening up the butterfly valve in the combustion-air supply main.

This method of regulation is based on the assumption of a constant relation at all times between the amount of air needed to make a given quantity of gas, and the amount of air needed to burn this same quantity. It must, of course be admitted that this regulation can only be 100 per cent. correct for one given quality of gas, and that it will become more or less incorrect as the quality of the gas changes. It must be kept in mind that the gas producers will receive their air under fan pressure, and that a constant relation between air and steam is always maintained by watching the temperature of the air-steam mixture. If desired, the saturation temperature of the producer air can be automatically maintained constant. This has so far not been found necessary, as it was possible to choose a turbine of such steam consumption that the exhaust steam was kept in a very close relation to the quantity of air delivered by the fan. The result is a much more uniform gas than is usually obtained from producers that are blown with steam jet blowers.

There is no excuse for really large changes in the quality of the gas from producers equipped in this manner. If the height of the fuel bed is carefully watched by frequent use of measuring sticks, if the producer, when it happens to need poking, is throttled down, for which purpose blast gates are supplied in the air leg to each producer; if, finally, the poking of the producer is generally done while the furnace is being tapped and charged; then there is no excuse for larger variations in the quality of the gas than about 10 B. t. u. per cu. ft. and then only for short periods

during the poking time. Such small variations will not in any serious way affect the correctness of the regulation.

Generally speaking, of course, it can not be claimed that automatic regulation applied to existing open-hearth furnaces can ever be 100 per cent. perfect. Although every effort is made to eliminate air infiltration into the checker chambers and the uptakes by suitable regenerator covering, such air infiltrations cannot entirely be avoided. On the other hand, it has been ascertained by careful measurements that between 85 and 90 per cent. of the total combustion air is actually being regulated, whereas only 10 to 15 per cent. passes into the furnace as infiltrated air without being regulated. Although the desirability of regulating all the combustion air is self evident, the error in allowing 15 per cent. to pass in unregulated, is not very serious because the infiltrated air usually remains constant. By means of flue-gas analyses the regulation is set for the largest quantity of gas needed during melting. If the regulation is fully correct for this largest quantity, then, of course, as the gas supply to the furnace is cut down, the infiltrated air will bring about a certain small excess of air. In view of the fact that this cutting down of the gas to the furnace generally coincides with the reaction period of the bath, where additional quantities of air are necessary in order to burn the CO generated by the bath, this infiltrated air often obviates the need of changing the orifice plate on the combustion-air intake box during the refining period, as is borne out by Tables 7 and 8.

RESULTS FROM REGULATION

Combustion

The use of straight coke-oven gas on open-hearth furnaces has for a long time been considered inadvisable, because the flame of coke-oven gas has a rather low visibility, also because furnaces operated on such gas alone showed a distinct tendency towards foaming. The low visibility is not by any means a serious factor. Experience has shown that the helpers will soon get accustomed to the flame of straight coke-oven gas. Where visibility is nevertheless desired, a little tar or oil, say one or two gallons per ton of steel, will produce visibility without interfering with the regulation.

The problem of the foaming was approached with much misgiving. Accordingly it was a very agreeable surprise to find no foaming problem with regulated combustion on furnaces fired with straight coke-oven gas. The explanation for the fact that no foaming took place, may be found in the much more uniform temperatures that are being maintained in an open-hearth furnace with automatic control. This would tend to show that the foaming may be due to a temporary decrease in the temperature of the furnace, resulting in a cooling of the slag on top of the bath, which then, on account of its increased viscosity, will lose part of

its heat conductivity, with a consequent reduction of the activity of the bath. The heat transfer from the flame of coke-oven gas, probably because it contains very little free-burning carbon, does not appear to be strong enough to break through the foam and restore the activity of the bath. From experience of nearly two years, it appears to be safe to assume that foaming is the result of poor combustion, and that with controlled combustion, it seldom happens. In any case, the fear of foaming should not prevent the use of straight coke-oven gas as open-hearth fuel and the advantage of positive automatic control. If burners suitable for coke-oven gas and tar are adopted, tar can always temporarily be put on the furnace to break up foaming, should it occur.

Straight coke-oven gas has proved an ideal fuel for open-hearth furnaces, provided its combustion is always properly controlled. Furnaces have thereby been very considerably speeded up and at the same time cost of repair has been greatly reduced and the life of the furnace has been increased.

Table 7 shows a number of combustion analyses taken during one heat on a furnace equipped with automatic control and using coke-oven gas. It very clearly shows to what extent control of combustion is possible. The increase in oxygen towards the end of the heat, when very much smaller quantities of gas are passing through the furnace, illustrates the effect of infiltrated unregulated air.

Automatic regulation on a furnace fired with producer-gas improved the quality of the gas very much. A number of analyses taken during one month showed a lowest B. t. u. value of 147 and a highest of 154 B. t. u. as against other producers not controlled with a lowest value of 115 and a highest of 150 B. t. u. The combustion results compared favorably with those from coke-oven gas as is shown by Table 8 which gives some waste-gas analyses taken during one heat. As the flow of gas in this instance could not be ascertained, we give the various differential air pressures of the producer air. The variations in the quantities from hour to hour are not as evident as in a furnace fired with coke-oven gas, because when these analyses were taken the furnace was already rather old and could not be forced, as would have been possible with a new furnace.

Table 9 proved very useful in compiling these data.

Production and Fuel Consumption

In order to prove the speeding up of the furnaces and the consequent saving of fuel, we have observed, from April to November, 1925, inclusive, seven 100-ton open-hearth furnaces. In three of the furnaces, Nos. 5, 6, and 7, combustion was controlled; No. 5 was fired with producer gas and Nos. 6 and 7 with straight coke-oven gas. Of the other four furnaces,

which were not controlled, No. 1 was fired with producer gas, Nos. 2 and 4 with tar and coke-oven gas, and No. 3 part of the time with tar and coke-oven gas and part with straight producer gas. Of the three controlled furnaces, No. 5 was controlled only for three months, whereas Nos. 6 and 7 were continually under control. The compilation of production for each furnace omits all the repair months; therefore, the observations cover 47 months of production for seven furnaces. We can then compare operation of producer-gas furnaces for 15 months without control with 3 months with control, and operation for 15 months with coke-oven gas and tar without control with 14 months with control. The comparative figures are as follows:

Furnaces Fired with Producer Gas

- (a) Without control: Production during 15 operation months 86,897 tons, or 5,790 tons per month per furnace.
- (b) With control: Production during 3 operation months 19,874 tons, or 6,625 tons per month per furnace.

Furnaces Fired with Coke-oven Gas and Tar

- (a) Mixed tar and coke-oven gas without control: Production during 15 operation months 92,398 tons, or 6,160 tons per month per furnace.
- (b) Straight coke oven gas with control: Production during 14 operation months 96,311 tons, or 6,870 tons per month per furnace.

With regard to the last figure, it will be interesting to note that for the last 5 operation months, the production went up to 35,978 tons, or 7,195 tons per month. The above figures clearly show the large increase in production; the controlled furnaces actually delivered an average of two heats per week more than the uncontrolled furnaces.

With regard to the furnace No. 5 which has the installation controlling producer gas, it must be remembered that the three months of observation were the last three months before rebuilding. Since then the furnace was rebuilt and was in operation again at the end of November. The figures for the first 18 days in December showed that the furnace made 42 heats, producing 4,304 tons of steel with a coal consumption of 445 lbs. per ton of steel. At this rate of production, the furnace would make in December 7,250 tons of steel, which would exceed the best figures for straight coke-oven gas. It will be remembered that the calculations in Table 6 showed that producer gas should give slightly better results than coke-oven gas.

In compiling the fuel figures, we were under a rather serious handicap, as we could not compile the fuel consumption for all the months for which we had the production figures. We have, however, consumption figures for 11 operation months on producer-gas furnaces without combustion control and for 3 months with combustion control; also for 13 operation

months firing with coke-oven gas and tar without control and for 10 months using straight coke-oven gas with control. The comparative figures are as follows:

Furnaces Fired with Producer Gas

- (a) Without control: During 11 operation months 62,283 tons of steel were produced with a consumption of 34,200,000 lbs. of coal, equivalent to 550 lb., or 7.47 million B. t. u., in the coal per ton of steel.
- (b) With control: During 3 operation months 19,874 tons of steel were produced, using 10,200,000 lb. of coal, or a coal consumption of 513 lb., or 6.93 million B. t. u., in the coal per ton of steel.

Although the above figures showed a considerable increase in production, the fuel consumption was not reduced as much as one would expect, because the regenerators were already very old and interference of the preheat was serious. As has already been stated, the run on the rebuilt furnace shows not only a very much larger production, but also a reduction of fuel consumption to 449 lb. of coal, or 6.11 million B. t. u., per ton of steel in the coal.

Furnaces Fired with Coke Oven Gas and Tar

- (a) Without control: During 13 operation months 79,225 tons of steel were made with a heat consumption of 573,830 million B. t. u. in gas and tar, or 7.25 million B. t. u., per ton of steel.

(In order not to complicate the above calculations we did not separate the gas and the tar.)

- (b) Straight coke-oven gas with control.

(Separate figures are given for furnaces Nos. 6 and 7 because No. 6 was equipped with the latest type of control and therefore gave much better results.)

(1) Furnace No. 6.—During 6 operation months 39,215 tons of steel were produced with a gas consumption of 351.0 million cu. ft., *i. e.* 8,950 cu. ft., or 4.42 million B. t. u., per ton of steel.

(2) Furnace No. 7: During 4 operation months 28,207 tons of steel were produced with a gas consumption of 293.35 million cu. ft. of coke oven gas, *i. e.*, 10,370 cu. ft. of gas, or 5.12 million B. t. u., per ton of steel.

Life of Furnace and Rebuilding Costs

Regarding the saving in the life of the furnace, no figures so far are available on controlled furnaces fired with producer gas, because no complete set of tests has yet been made with a controlled furnace. With the two coke-oven gas furnaces, we have so far made only two complete sets of tests. The longest run was on No. 6 furnace with 409 heats, pro-

ducing 42,334 tons of steel. The total rebuilding cost for this furnace was as follows:

Bricklayers.....	\$ 480.00	
Helpers.....	273.70	
Loading brick.....	144.44	
General labor.....	1176.56	
Silica clay.....	72.00	
Fireclay.....	33.00	
Brick.....	6359.44	\$8539.14

The cost was approximately 20c. per ton of steel. Unfortunately exact figures as to the cost of the intermediate repairs during the run of the furnace are not available, but it is estimated at not more than an additional 20c. per ton of steel, so that the repair cost does not appear to exceed 40c. per ton of steel.

The No. 5 producer-gas furnace was also rebuilt after controlled combustion for about one-half of the campaign. It made during the whole run 341 heats and produced 34,808 tons of steel. The previous run without control was 279 heats, producing 29,023 tons of steel. The rebuilding cost after the run of 341 heats were: -

Labor.....	\$2870.82	
Store.....	208.75	
Brick.....	5082.03	
Fireclay.....	38.72	\$8195.32

The cost therefore amounted to approximately 28c. per ton of steel.

IMPORTANCE OF CONTINUOUS FUEL SUPPLY

Stress should be laid on the importance of a continuous fuel supply, not only to speed up the operation of the furnace, but also materially to decrease the fuel consumption.

When No. 7 furnace was first equipped for straight coke-oven gas with combustion control, the gas mains carrying the gas to the furnace were so small that high pressures were needed to force enough gas through them to the ports. In order to maintain these pressures, it was necessary to cut off the gas from all other furnaces, with the result that vast quantities of gas were bled. For about 12 days, this condition of very uniform gas pressure lasted. Then the small gas mains were replaced by much larger mains and the gas was distributed to many furnaces. This distribution resulted in marked irregularity of the gas pressure, because of the constantly changing demand on the gas supply. During these first 12 days, the gas consumption on No. 7 furnace was remarkably low, varying

between 6,200 and 6,500 cu. ft. of gas per ton of steel. As soon as the larger gas mains had been installed and the gas pressure became irregular, this consumption increased to about 10,000 cu. ft. of gas per ton of steel, where it has since been held. At the time the author was unable to find any explanation for this sudden change in gas consumption and, therefore, came to the conclusion that the meter readings during the first 12 days must have been wrong, although an examination by the meter manufacturers did not reveal anything amiss. In September, 1925, a similar condition was created. When No. 6 furnace was being rebuilt, the other furnaces were unable to take the whole of the coke-oven gas, and gas had to be bled. During rebuilding when the gas pressure was always at 5 lb. or above, 17 heats were made, producing 1,802 tons of steel and using only 10,862,500 cu. ft. of gas, *i. e.* 6,028 cu. ft. of gas, or 3,134,560 B. t. u., per ton of steel.

As the low gas consumption was restored as soon as the conditions that prevailed during the first regulation period were restored, one would hardly be justified in discarding the results obtained during this second period as due to erroneous gas readings. The explanation will probably lie in the fact that the heat transfer in an open-hearth furnace is overwhelmingly due to radiation. As the radiation increases and decreases in the relation of the fourth power of the differences of the absolute temperatures, and as the working range of temperatures in an open-hearth furnace, which is between 3000° and 3200° F., is so limited, it is certainly quite conceivable that continuous changes up and down in the temperatures obtained may have a decided influence on the rate of heat transfer and, therefore, on the speed and fuel consumption of the furnace. If this should be true, the experience related above would be an extremely strong argument for a gas holder in connection with every coke-oven gas-fired open-hearth plant. It is regrettable that the author heard of this astonishingly favorable run only after the conditions under which it was possible had ceased to exist, so that the necessary data to prove the possibility of this low fuel consumption could not be collected. Generally speaking, of course, Table 6 shows that low fuel consumptions of this kind are not by any means impossible, even with open-hearth furnaces of the present customary design.

CONCLUSIONS

The author emphasizes the necessity of a large number of exact heat-balance sheets under varying conditions, laying special stress on the need of particular care in temperature measurements.

Preheating temperatures for the present type of checker chambers are naturally low and on new construction, particular care should be taken not only to increase the size of the checker chamber, but also to obtain

even distribution of outgoing and ingoing gases over all parts of the checker chambers.

The results obtained from an open-hearth furnace depend on the amount of gas completely burned for a given period, and on as low an excess of air as is possible. This necessitates the installation of forced-draft and induced-draft fans and equipment with automatic combustion control.

ACKNOWLEDGMENT

Appreciation is hereby expressed for the care and interest taken by all participants in this work in observation, tabulation and making drawings.

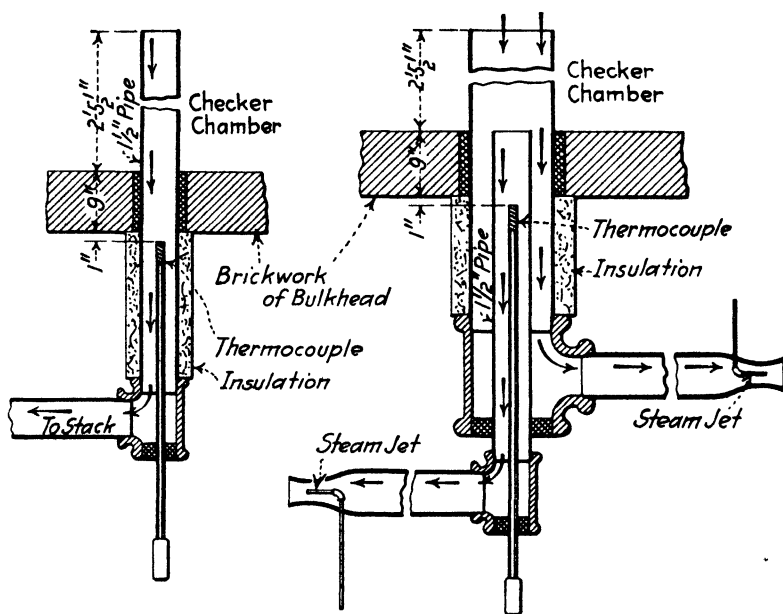


FIG. 1.

FIG. 2.

FIG. 1.—ARRANGEMENT OF RADIATION WITH PROTECTED PYROMETERS AS USED.

FIG. 2.—ARRANGEMENT OF RADIATION WITH PROTECTED PYROMETERS AS RECOMMENDED.

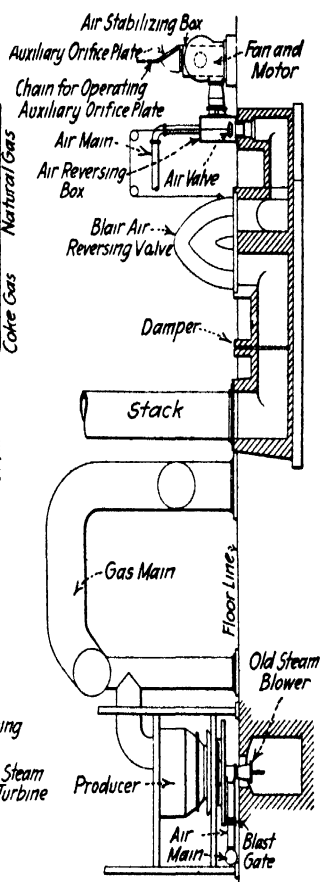
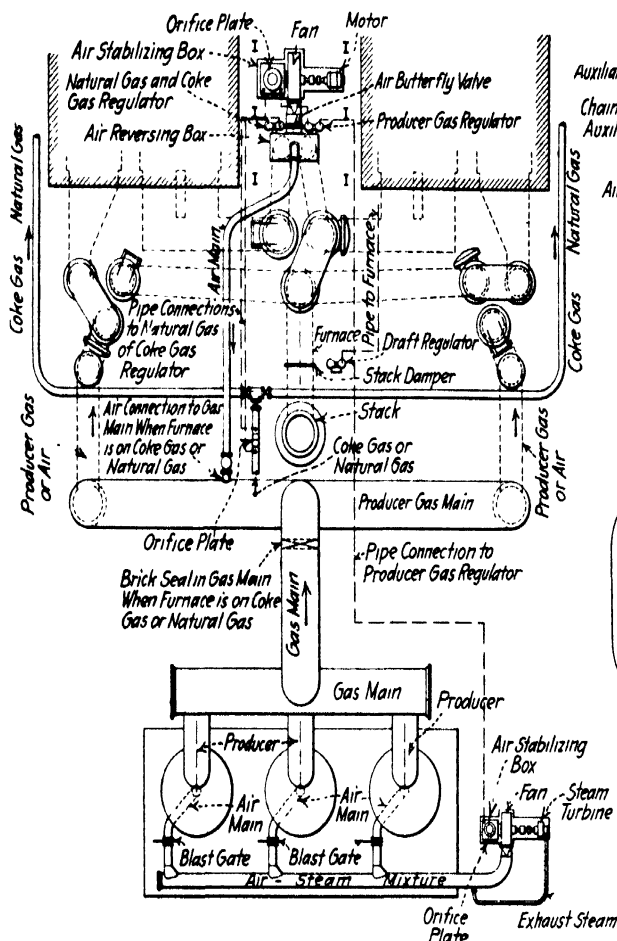


FIG. 3.—PLAN. FIG. 4.—SECTIONAL ELEVATION
GENERAL LAYOUT OF INSTALLATION FOR NATURAL GAS, COKE-OVEN GAS OR
PRODUCER GAS FIRING.

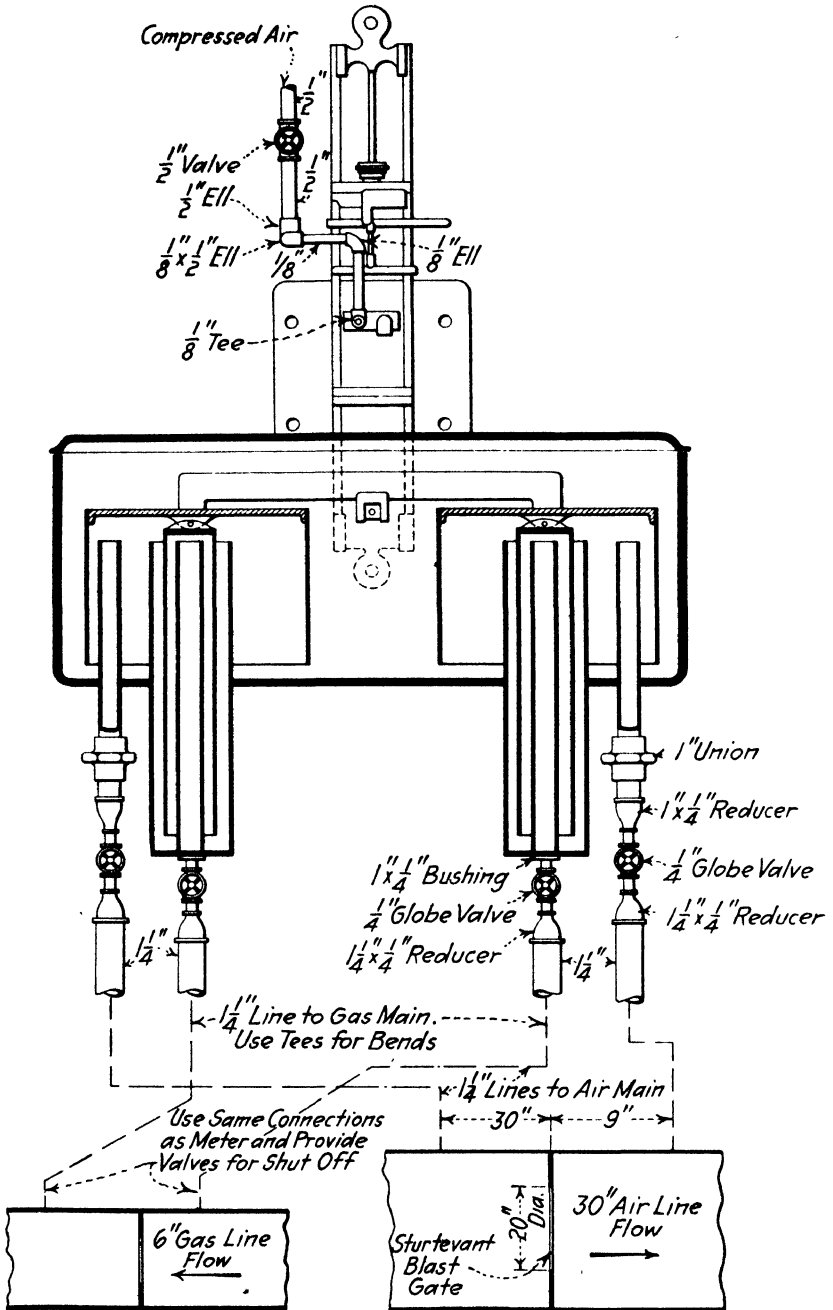


FIG. 5.—SECTION OF HUESSENER COMBUSTION REGULATOR.

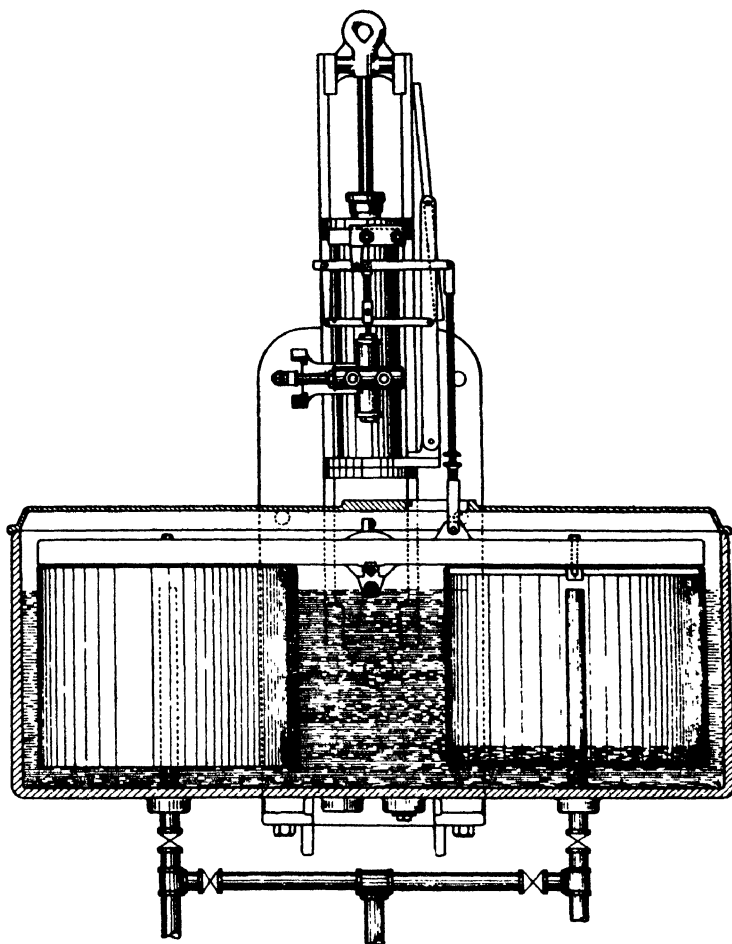


FIG. 6.—SECTION OF COMBUSTION REGULATOR FOR PRODUCER-GAS FURNACE.

TABLE-2.
HEAT CONTENT OF PRODUCTS OF COMBUSTION.

WHEN COMBUSTION AIR IS IN EXCESS	FROM VARIOUS FUELS, EACH CONTAINING ONE MILLION B.T.U. LATENT HEAT.										HEAT CONTENT MEASURED ABOVE 32°F.				
	AT VARIOUS TEMPERATURES.														
	FROM VARIOUS FUELS, EACH CONTAINING ONE MILLION B.T.U. LATENT HEAT.														
	FROM 987 Cu.Ft. OF NATURAL GAS @ 1012 B.T.U. / Cu. Ft.		FROM 1870 Cu.Ft. OF COKE OVEN GAS @ 529 B.T.U. / Cu. Ft.		FROM 522 LBS. OF CRUDE OIL. @ 19210 B.T.U. / LB. (219 GALLONS @ 141,000 B.T.U.)		FROM 6660 Cu. Ft. OF DRY PINE GAS @ 150.3 B.T.U. / Cu. Ft. (FROM 93.7 LBS. COAL @ 1354 B.T.U.)		FROM 7350 Cu. Ft. DRY PROD. GAS @ 132.5 B.T.U. / Cu. Ft. (FROM 102.7 LBS. COAL @ 1354 B.T.U.)						
	B.T.U. IN PRODUCTS OF COMBUSTION		B.T.U. IN PROD. OF COMBUSTION		B.T.U. IN PROD. OF COMBUSTION		B.T.U. IN PROD. OF COMBUSTION		B.T.U. IN PROD. OF COMBUSTION		B.T.U. IN PROD. OF COMBUSTION				
	AT	AT	AT	AT	AT	AT	AT	AT	AT	AT	AT	AT	AT	AT	AT
	3000°	2300°	1250°	3000°	2300°	1250°	3000°	2300°	1250°	3000°	2300°	1250°	3000°	2300°	1250°
	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
0	769,000	572,000	292,000	739,000	538,000	280,000	693,000	528,000	270,000	947,000	708,000	362,000	996,000	739,000	378,000
5	801,000	596,000	304,000	769,000	569,000	291,000	723,000	550,000	282,000	973,000	727,000	372,000	1,021,000	759,000	388,000
10	832,000	619,000	317,000	798,000	582,000	303,000	753,000	572,000	293,000	998,000	747,000	382,000	1,047,000	777,000	398,000
15	864,000	643,000	329,000	827,000	604,000	314,000	783,000	595,000	305,000	1,023,000	766,000	392,000	1,072,000	796,000	407,000
20	896,000	667,000	341,000	856,000	625,000	325,000	812,000	617,000	316,000	1,050,000	785,000	402,000	1,097,000	815,000	417,000
25	927,000	690,000	353,000	885,000	647,000	337,000	842,000	639,000	326,000	1,076,000	804,000	412,000	1,123,000	833,000	427,000
30	959,000	714,000	366,000	915,000	669,000	348,000	872,000	662,000	339,000	1,102,000	823,000	422,000	1,148,000	852,000	437,000
35	991,000	738,000	378,000	944,000	691,000	359,000	902,000	684,000	351,000	1,127,000	843,000	432,000	1,173,000	871,000	447,000
40	1,023,000	761,000	390,000	973,000	713,000	371,000	931,000	706,000	362,000	1,153,000	863,000	442,000	1,199,000	890,000	456,000

TABLE - 3.
HEAT AVAILABLE FOR PREHEATING COMBUSTION AIR AND FUEL.
 DERIVED FROM THE COMBUSTION OF VARIOUS FUELS REFERRED TO 1-MILLION B.T.U. LATENT HEAT.
 ADMITTED FOR COMBUSTION FOR A TEMP. DROP FROM 2300 °F. TO 1250 °F.

EXCESS OF AIR, %	1890 Cu. Ft. Of Natural Gas @ 1012 B.T.U. / Cu. Ft.	1890 Cu. Ft. Of Coking Gas @ 524 B.T.U. / Cu. Ft.	52.2 LBS. OF CRUDE OIL, @ 19210 B.T.U. / LB.	6660 Cu. Ft. Of Dry Prod. Gas @ 150.3 B.T.U. / Cu. Ft.	7550 Cu. Ft. Of Dry Prod. Gas @ 132.5 B.T.U. / Cu. Ft.
1.	2.	3.	4.	5.	6.
0	280,000	258,000	258,000	346,000	361,000
5	292,000	269,000	268,000	355,000	370,000
10	302,000	279,000	279,000	365,000	379,000
15	314,000	290,000	290,000	374,000	389,000
20	326,000	300,000	301,000	383,000	398,000
25	337,000	310,000	311,000	392,000	406,000
30	348,000	321,000	323,000	401,000	415,000
35	360,000	332,000	333,000	411,000	424,000
40	371,000	342,000	344,000	420,000	434,000

[The material set in type in this and the following tables was supplied by the author subsequent to the presentation of the paper, February, 1926.]

For a Temperature Drop from 2300° F. to 1150°, 1050°, 950° and 850°, respectively

10	328,000	303,000	304,000	397,000	412,000
10	346,000	331,000	329,000	429,000	445,000
10	383,000	356,000	353,000	462,000	481,000
10	410,000	382,000	377,000	495,000	505,000

TABLE 4-A.
B.T.U. AVAILABLE IN BATH. (ABOVE 3000°F.).
FOR 1-MILLION B.T.U. LATENT HEAT ADMITTED
WITH VARYING EXCESS AIR AND AT VARYING TEMP. OF THE PREHEATED AIR
(THE FUEL BEING COLD.)

COMBUSTION AIR BEING PREHEATED TO --- °F.	FROM 987 CU. FT. OF COLD NAT. GAS.				FROM 1890 CU. FT. OF COLD COKE OVEN GAS				FROM 52.2 LBS. OF COLD CRUDE OIL.			
	WHEN COMBUSTION AIR IS IN EXCESS				WHEN COMBUSTION AIR IS IN EXCESS				WHEN COMBUSTION AIR IS IN EXCESS			
	0%	10%	20%	40%	0%	10%	20%	40%	0%	10%	20%	40%
NO PREHEAT. 32°	231,000	160,000	104,000	NONE.	261,000	202,000	144,000	27,000	307,000	247,000	180,000	69,000
1000 °F.	424,000	381,000	336,000	249,000	439,000	390,000	350,000	277,000	409,000	447,000	406,000	324,000
	511,000 (1430°)	470,000 (1390°)	430,000 (1350°)	349,000 (1300°)	519,000 (1420°)	481,000 (1380°)	444,000 (1340°)	369,000 (1300°)	565,000 (1390°)	526,000 (1370°)	489,000 (1360°)	413,000 (1330°)
1600 °F.	550,000	521,000	488,000	426,000	556,000	527,000	499,000	441,000	608,000	570,000	550,000	491,000
1900 °F.	613,000	590,000	564,000	515,000	615,000	592,000	569,000	524,000	668,000	644,000	621,000	574,000
2200 °F.	680,000	665,000	645,000	609,000	677,000	660,000	644,000	610,000	731,000	714,000	697,000	663,000

For a Temperature Drop from 2300° F. to 1150°, 1050°, 950° and 850°, respectively

496,000	505,000	551,000
(1500°)	(1500°)	(1490°)
514,000	533,000	576,000
(1580°)	(1630°)	(1590°)
551,000	558,000	600,000
(1730°)	(1750°)	(1700°)
578,000	584,000	624,000
(1850°)	(1870°)	(1800°)

TABLE 4-B.

B.T.U. AVAILABLE IN BATH (ABOVE 3000° F.).

FOR 1-MILLION B.T.U. LATENT HEAT IN DRY PRODUCER GAS OF 1000° F. ENTERING CHECKER CHAMBERS.
WITH VARYING EXCESSES OF AIR, PREHEATING AIR AND FUEL TO VARIOUS TEMPERATURES.

COMBUSTION AIR PREHEATED TO --- ° F.	RICH PRODUCER GAS. LATENT HEAT OF 6660 Cu.Ft. = 1,000,000 B.T.U. SENSIBLE HEAT OF 6660 Cu.Ft. (1000° F.) = 128,000 B.T.U.									
	PRODUCER GAS TEMPERATURE 1600° F. (PREHEATED BY 600° F.)					PRODUCER GAS TEMPERATURE 2200° F. (PREHEATED BY 1200° F.)				
	0%	10%	20%	40%	COMBUSTION AIR IN EXCESS.	0%	10%	20%	40%	COMBUSTION AIR IN EXCESS.
NO PREHEAT 32°	181,000	119,000	78,000	25,000	267,000	215,000	164,000	61,000	355,000	303,000
1000° F.	338,000	302,000	266,000	195,000	424,000	398,000	352,000	281,000	512,000	476,000
1600° F.	441,000	415,000	396,000	339,000	527,000	501,000	476,000	425,000	615,000	589,000
1900° F.	493,000	472,000	452,000	411,000	579,000	558,000	538,000	497,000	667,000	646,000
2200° F.	547,000	532,000	517,000	488,000	633,000	618,000	603,000	574,000	721,000	706,000

For a Temperature Drop from 2300° F. to 1150°, 1050°, 950° and 850°, respectively

TABLE 4-C.
B.T.U. AVAILABLE IN BATH (ABOVE 3000°F.)

FOR 1-MILLION B.T.U. LATENT HEAT IN DRY PRODUCER GAS OF 1000°F. ENTERING CHECKER CHAMBERS.
WITH VARYING EXCESSES OF AIR, PREHEATING AIR AND FUEL TO VARIOUS TEMPERATURES.

COMBUSTION AIR PREHEATED TO --- °F.	PRODUCER GAS TEMPERATURE 1000°F. (NOT PREHEATED)			PRODUCER GAS TEMPERATURE 1600°F. (PREHEATED BY 600°F.)			PRODUCER GAS TEMPERATURE 2200°F. (PREHEATED BY 1200°F.)		
	COMBUSTION AIR IN EXCESS.			COMBUSTION AIR IN EXCESS.			COMBUSTION AIR IN EXCESS.		
	0%	10%	20%	0%	10%	20%	0%	10%	20%
NO PREHEAT 32°									
1000°F.	150,000	49,000	49,000	NONE.	255,000	204,000	349,000	299,000	248,000
	304,000	269,000	234,000	163,000	409,000	374,000	503,000	468,000	433,000
						478,000	511,000	478,000	447,000
1600°F.	405,000	380,000	356,000		511,000	(1320°)	(1830°)	(1660°)	(1080°)
1900°F.	456,000	435,000	416,000		561,000	(1540°)	(1730°)	(1660°)	
		478,000	447,000						
		(2120°)	(2050°)						
2200°F.	510,000	495,000	481,000	450,000	615,000	600,000	655,000	634,000	555,000
	511,000						709,000	694,000	600,000
	(2210°)								

For a Temperature Drop from 2300° F. to 1150°, 1050°, 950° and 850°, respectively

	511,000
	(1730°)
	544,000
	(1920°)
	580,000
	(2100°)
	604,000
	(2220°)

TABLE-5.
LATENT HEAT IN FUEL TO BE SUPPLIED FOR COMBUSTION TO A 100 T. OPENHEARTH FURNACE
FOR MAKING 1-TON OF STEEL
FOR VARYING DURATION OF A HEAT AND VARYING EXCESS OF THE COMBUSTION AIR
CONSIDERING THE ACTUAL HEAT LOSSES OF THE PROCESS AND ACTUAL WORKING CONDITIONS REQUIRED ABOVE 3000°F.

WHEN COMBUSTION AIR IS IN EXCESS %	MILLIONS B.T.U. IN NAT. GAS. (CUB. FT. OF GAS @ 1012 B.T.U.)			MILLIONS B.T.U. IN COKE GAS. (CUB. FT. OF GAS @ 529 B.T.U.)			MILLIONS B.T.U. IN CRUDE OIL (GALLONS @ 141,000 B.T.U.)			MILLIONS B.T.U. IN RICH PRODUCE GAS (LBS. OF COAL @ 13500 B.T.U.)			MILLIONS B.T.U. IN POOR PRODUCE GAS (LBS. OF COAL @ 13500 B.T.U.)		
	DURATION OF HEAT 12 HRS. 10 HRS. 8 HRS.	DURATION OF HEAT 12 HRS. 10 HRS. 8 HRS.	DURATION OF HEAT 12 HRS. 10 HRS. 8 HRS.	DURATION OF HEAT 12 HRS. 10 HRS. 8 HRS.	DURATION OF HEAT 12 HRS. 10 HRS. 8 HRS.	DURATION OF HEAT 12 HRS. 10 HRS. 8 HRS.	DURATION OF HEAT 12 HRS. 10 HRS. 8 HRS.	DURATION OF HEAT 12 HRS. 10 HRS. 8 HRS.	DURATION OF HEAT 12 HRS. 10 HRS. 8 HRS.	DURATION OF HEAT 12 HRS. 10 HRS. 8 HRS.	DURATION OF HEAT 12 HRS. 10 HRS. 8 HRS.	DURATION OF HEAT 12 HRS. 10 HRS. 8 HRS.	DURATION OF HEAT 12 HRS. 10 HRS. 8 HRS.	DURATION OF HEAT 12 HRS. 10 HRS. 8 HRS.	DURATION OF HEAT 12 HRS. 10 HRS. 8 HRS.
1	2 3 4	2 3 4	2 3 4	2 3 4	2 3 4	2 3 4	2 3 4	2 3 4	2 3 4	2 3 4	2 3 4	2 3 4	2 3 4	2 3 4	2 3 4
0	4.4 (4350)	4.0 (3760)	3.6 (3570)	4.35 (8150)	3.95 (7410)	3.55 (6600)	4.0 (20.2)	3.65 (25.7)	3.25 (23.1)	4.3 (400)	3.9 (365)	3.5 (330)	4.4 (450)	4.0 (410)	3.6 (370)
10	4.8 (4700)	4.35 (4240)	3.9 (3870)	4.7 (8770)	4.25 (7990)	3.85 (7210)	4.25 (20.2)	3.9 (27.5)	3.5 (24.8)	4.55 (425)	4.15 (390)	3.75 (350)	4.7 (480)	4.3 (440)	3.85 (395)
20	5.2 (5130)	4.75 (4670)	4.3 (4230)	5.05 (9530)	4.6 (8680)	4.15 (7820)	4.6 (22.5)	4.2 (29.6)	3.75 (26.7)	4.9 (460)	4.45 (415)	4.0 (375)	5.0 (510)	4.6 (470)	4.1 (420)
40	6.4 (6320)	5.85 (5760)	5.25 (5190)	6.1 (1150)	5.5 (1040)	5.0 (9430)	5.45 (20.5)	4.95 (36.1)	4.45 (31.6)	5.7 (535)	5.2 (485)	4.65 (435)	5.9 (605)	5.4 (555)	4.85 (495)

For a Temperature Drop from 2300° F. to 1150°, 1050°, 950° and 850°, respectively

10	4.52	4.11	3.71	4.42	4.03	3.64	4.07	3.70	3.34	4.26	3.88	3.50	4.39	4.0	3.6
10	4.36	3.97	3.58	4.21	3.83	3.45	3.89	3.54	3.20	4.01	3.65	3.30	4.12	3.75	3.38
10	4.07	3.70	3.34	4.02	3.66	3.30	3.73	3.40	3.07	3.79	3.45	3.11	3.86	3.52	3.17
10	3.88	3.49	3.18	3.84	3.49	3.15	3.59	3.27	2.95	3.59	3.27	2.95	3.71	3.38	3.04

TABLE - G.
AVERAGE RATE OF FLOW OF FUEL TO BE COMPLETELY BURNED IN A 100 t. OPEN HEARTH FURNACE.
FOR MAKING A 100 t. HEAT
FOR VARYING DURATION OF A HEAT AND AT VARYING EXCESS OF THE COMBUSTION AIR.
CONSIDERING THE ACTUAL HEAT LOSSES OF THE PROCESS AND ACTUAL WORKING CONDITIONS REQUIRED (ABOVE 3000°F).

WHEN COMBUSTION AIR IS IN EXCESS %	NATURAL GAS IN CU. FT. / HR.			COKE GAS IN CU. FT. / HR.			OIL IN GALLONS / HR. 1-GAL. = 7.34 LBS. = 141,000 BTU			RICH PROD. GAS IN CU. FT. / HR. (IN LBS. OF COAL / HR.)			POOR PROD. GAS IN CU. FT. / HR. (IN LBS. OF COAL / HR.)		
	DURATION OF HEAT			DURATION OF HEAT			DURATION OF HEAT			DURATION OF HEAT			DURATION OF HEAT		
	12 HRS.	8 HRS.	4	12 HRS.	8 HRS.	4	12 HRS.	8 HRS.	4	12 HRS.	8 HRS.	4	12 HRS.	8 HRS.	4
	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
0	36,000	40,000	44,400	66,000	75,000	84,000	236	259	288	259,000 (3330)	260,000 (3650)	291,000 (4120)	277,000 (3750)	302,000 (4100)	339,000 (4,500)
10	40,000	43,000	48,100	74,000	80,000	89,000	251	277	310	252,000 (3540)	276,000 (390)	312,000 (4370)	295,000 (400)	324,000 (440)	363,000 (4940)
20	43,000	47,000	53,100	80,000	87,000	98,000	272	298	332	272,000 (3830)	296,000 (4150)	332,000 (4600)	314,000 (440)	347,000 (4700)	386,000 (5250)
40	53,000	59,000	64,800	96,000	104,000	129,000	322	351	394	316,000 (4460)	346,000 (4850)	387,000 (5450)	371,000 (5040)	407,000 (5550)	457,000 (6100)

TABLE - 7.

#6 O.H. FURNACE. COKE OVEN GAS WITH COMBUSTION CONTROL.

HEAT #6644 MARCH 14th. 1925.

WASTE GAS ANALYSIS.

		ANALYSIS			GAS FLOW CUFT/HR.
		CO ₂ %	O ₂ %	CO. %	
BEGAN CHARGING	8 ⁰⁰ AM.				
SCRAP	8 ¹⁰	10.0	1.0	—	115,000
FINISHED CHARGING.	9 ⁰⁰ AM.				
SCRAP.	9 ¹⁰	9.9	1.2	—	115,000
	10 ⁰⁰ AM	9.7	1.3	—	110,000
		10.1	1.2	—	115,000
	11 ⁰⁰ AM	8.9	.8	—	110,000
		9.1	1.0	—	115,000
	12 ⁰⁰ Noon	9.0	1.3	—	115,000
FINISHED CHARGING	12 ⁴⁵				
HOT METAL.	1 ⁰⁰ PM	13.0	1.6	.7	120,000
	2 ⁰⁰ PM	12.0	2.0	—	100,000
		10.0	2.2	—	75,000
	3 ⁰⁰ P.M.	10.2	2.5	—	80,000
		9.0	3.0	—	55,000
ORE ADDITION	4 ⁰⁰ P.M.	9.2	3.3	—	60,000
		8.0	3.0	—	55,000
	5 ⁰⁰ P.M.	9.0	3.0	—	55,000
		9.0	3.5	—	55,000
	6 ⁰⁰ PM	10.0	2.9	—	70,000
TAPPED					

TABLE - 8.

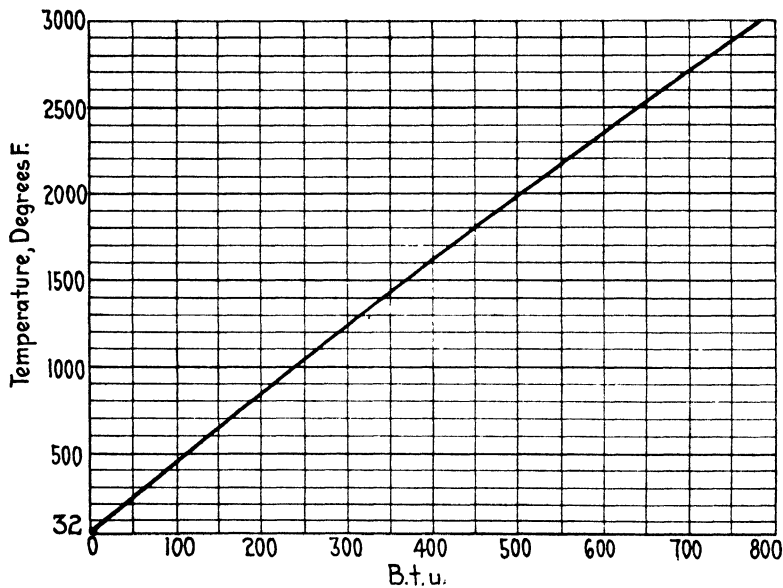
#5. O.H. FURNACE. PRODUCER GAS WITH COMBUSTION CONTROL

HEAT #5047 SEPT. 1ST, 1925.

WASTE GAS ANALYSIS.

	ANALYSIS.			DIFFERENTIAL PRESSURE OF AIR TO PRODUCERS W.G.
	CO ₂ %	O ₂ %	CO %	
8 ⁰⁰ A.M.				
BEGAN CHARGING 8 ¹⁰				
SCRAP.				
9 ⁰⁰ A.M.				
FINISHED CHARGING. 9 ³⁵				
SCRAP.				
10 ⁰⁰ A.M.	16.0	.2	.2	3.0"
	17.0	.4	—	2.8"
	16.7	.3	.3	2.7"
	18.2	1.3	—	3.0"
	17.3	.2	.6	2.9"
11 ⁰⁰ A.M.	17.1	.3	.7	2.8"
	18.2	.5	.9	2.9"
	17.5	.5	.3	2.7"
12 ⁰⁰ Noon				
FINISHED CHARGING 1 ⁰⁰ P.M.				
HOT METAL.				
2 ⁰⁰ P.M.				
	17.3	.7	.3	2.8"
	16.7	.2	.3	2.7"
3 ⁰⁰ P.M.	15.6	—	1.1	2.7"
	15.5	—	.8	2.6"
	17.5	.5	—	2.7"
4 ⁰⁰ P.M.	17.0	—	.2	2.8"
TAPPED. 5 ⁰⁰ P.M.				
5 ²⁵				
6 ⁰⁰ P.M.				

TABLE 9.—*Heat Content (Above 32° F.) in B. t. u. of 1 Lb. of Dry Air*



Elimination of Metalloids in the Basic Open-hearth Process

BY J. L. KEATS, WILMINGTON, DEL.,* AND C. H. HERTY, JR.,† LACKAWANNA, N. Y.

(New York Meeting, February, 1926)

IN THE literature on the elimination of metalloids in basic open-hearth practice, there are a great many heats recorded in which excellent data on changes in slag and metal composition during refining are given, but in almost all of these heats either temperature data or weights and analysis of charge are unrecorded and observations on the physical characteristics of the slag are almost always lacking. With these points in mind, a test heat was made in which as complete data as possible on all the factors that affect the elimination of metalloids were obtained.

THE TEST HEAT

The test heat was made in a standard 100-ton stationary furnace at the Lackawanna Steel Co., Lackawanna, N. Y., on January 17, 1922.

The Charge—Scrap.—The scrap consisted entirely of rail-heat butts, selected from a number of heats made the week before the test. The average analysis of the scrap was calculated from the analysis of these heats and from the weight of scrap from each heat.

Pig Iron.—Two ladles of pig iron were used in the charge and two samples were taken from each ladle as it was poured into the furnace. These four samples were composited for the average pig-iron sample.

Other Materials.—Weights of dolomite, ore and spar were obtained by weighing a quantity of each just before the test and weighing the amount of each left after the heat was completed. The limestone was weighed on the charging pans. Coal for recarburizing, ferromanganese, ferro-silicon and aluminum were weighed out as used. All these materials were carefully sampled before the test was begun. Coal consumption at the producers was obtained by getting the average capacity of the hoppers that fed the producers, and then counting the number of hoppers of coal used during the course of the heat.

Products

Steel.—The steel made was rolled into billets, the rolling properties being very satisfactory. The weight of steel was obtained by taking a

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tare weight on the ladle before tapping and then summing up the weights of the ingots, drainings and difference between the final and tare ladle weights (to obtain the weight of the skull).

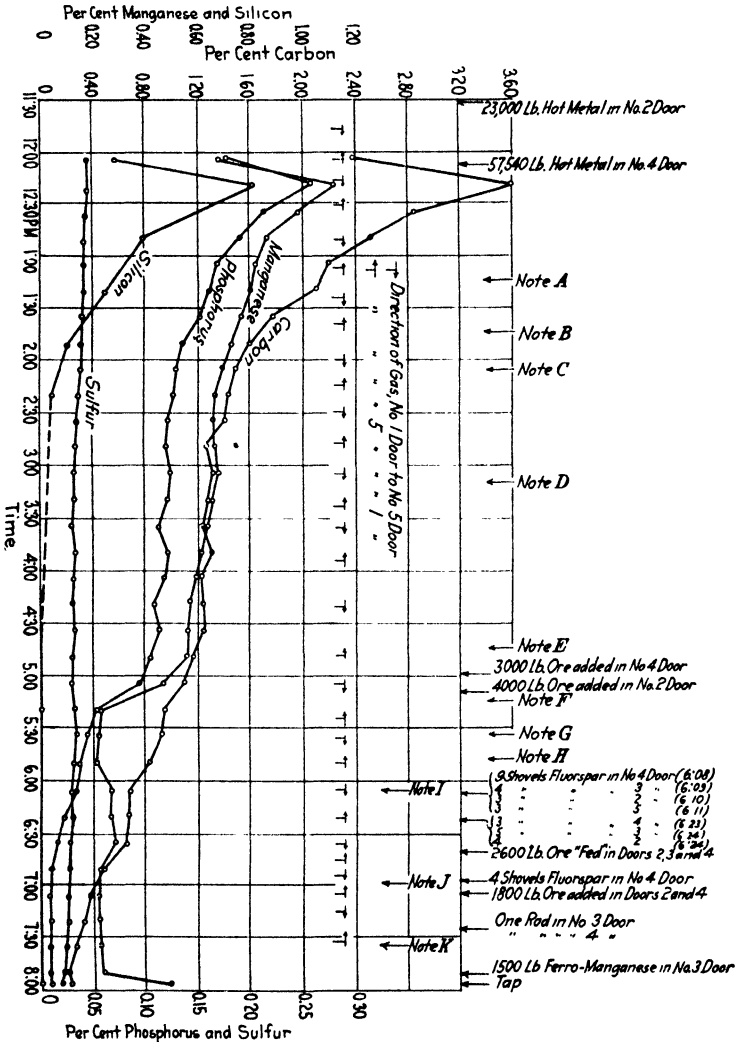


FIG. 1.—VARIATION IN COMPOSITION OF METAL FROM HOT METAL ADDITION TO TAP.

Slag.—The slag was collected in tared slag ladles, and was weighed in them.

Temperatures

The temperature of the slag in the furnace was taken with a Leeds and Northrup optical pyrometer. Temperatures were taken in all five doors. The temperatures found in the middle door, No. 3, are shown in

Fig. 18. Reversals, indicated by arrows on Fig. 1, show the gas flowing in the direction indicated by the arrow, *i. e.*, left to right or vice versa.

Sampling of Metal and Slag

Metal and slag samples were taken at 15-min. intervals at the three working doors of the furnace, starting as soon as there was enough molten material on the hearth to permit sampling.

The metal samples were drawn first and poured into ordinary break-test molds. Within half a minute, the corresponding slag samples were drawn and poured on iron plates. Both metal and slag samples were allowed to cool and were then marked for identification. Special precautions were taken to be sure that the samples from the three doors were taken simultaneously and that the time interval between samples was as close to 15 min. as possible.

The furnace doors were arbitrarily numbered from left to right, door No. 1 being at the left end of the furnace. The samples were designated by the sample number followed by a dash and the door number; thus 21-3 would be the twenty-first sample, door No. 3.

Note A.—Metal boiled vigorously around and on the outer edge of the mounds of pasty semi-molten scrap. Some lime lumps floated to the surface along the front wall. A collection of kish¹ still hung on the front bank at No. 4 door, remaining from the last ladle of metal which was poured in at that door.

Note B.—A vigorous boiling action continued on the mound of scrap at No. 2 door.

Note C.—At this time the slag had quite an appreciable amount of lime floating on its entire surface. The heat had the appearance of melting high in carbon, *i. e.*, the slag contained hard sharp-edged lumps of lime and the metal was dark in color.

Note D.—Lime is boiling up over the entire bath. Several lumps of scrap still above the level of the bath. The furnace was being run at a low temperature and the lime of the slag was softening up somewhat. The fluid portion of the slag was getting thicker.

Note E.—Lime was still boiling up in No. 3 door. Both ends were rather quiet, appearing as though the lime were all up in each end. The furnace and bath were quite cool and the slag was very viscous. The steam pressure was raised at this point to increase the volume of gas and thus raise the temperature, and thereby hasten the boiling up of the last of the lime.

Note F.—The slag dissolved the ore at once and a vigorous action took place throughout the entire bath.

Note G.—The temperature of the bath was rising; the slag was more fluid; and the general action of the bath more open.

Note H.—The slag was still frothing from ore addition.

Note I.—The lime was still boiling up at No. 3 door. The slag was of good consistency.

Note J.—Lime boil ceased and lime was apparently all up. The slag was a little heavy.

Note K.—Slag still showed the effects of the two recent ore additions. The rods stirred through the heat served to settle the frothing.

¹ Kish is residue from molten pig iron.

OPERATION OF HEAT

After tapping the previous heat the bottom was thoroughly drained and cleaned, three rabbles being used. The order of charging was as follows:

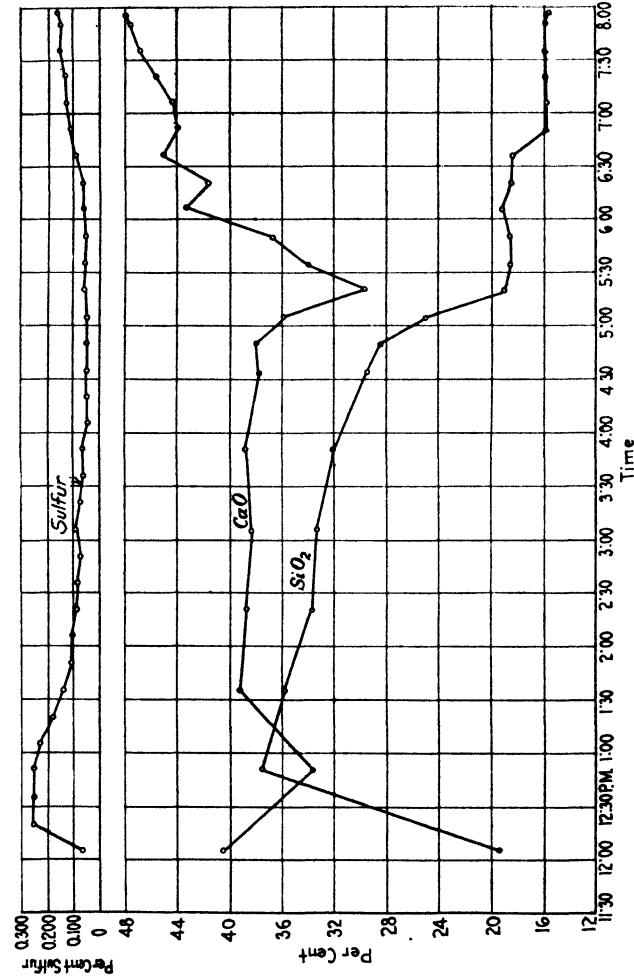


FIG. 2.—VARIATION IN SLAG COMPOSITION FROM HOT METAL ADDITION TO TAP.

TIME, A.M.	CHARGED
8:23-8:31	2700 lb. dolomite on back wall
8:39-8:47	26,000 limestone
8:52-9:01	1570 lb. dolomite on front wall
9:06-9:20	175,000 lb. scrap

At 11:34 the first ladle of pig iron was poured into the furnace, in No. 2 door. The reaction of this iron with the oxides formed during melting was rather light whereas the reaction from the second ladle, poured at

12:14 a.m. in No. 4 door, was much heavier. During the period 12:21 to 1:05 no samples could be taken from No. 4 door on account of a large amount of "kish" just inside the door. At 1:15 lime began to show up on the slag and by 2:05 the slag had an appreciable amount of lime floating over its entire surface. The metal at this time was boiling vigorously

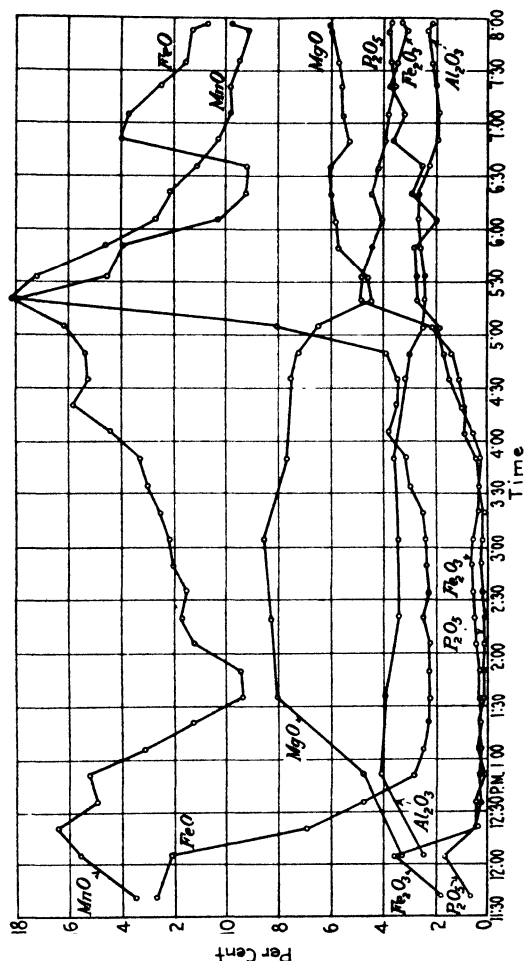


FIG. 3.—VARIATION IN SLAG COMPOSITION FROM HOT METAL ADDITION TO TAP.

on the mounds of scrap. At 3:20 the slag began to thicken and the lime was boiling up over the entire bath. At 4:45 the slag was very viscous and in both ends the lime was apparently "all up." Lime was still boiling in the middle door. At 5 o'clock, 3000 lb. of ore was added and 4000 lb. at 5:10. A vigorous action took place on the addition of this ore, the lime began to dissolve rapidly and the slag became more fluid.

As more lime was dissolved, the slag thickened up somewhat and elimination of carbon and phosphorus practically ceased.

The heat was sparred at 6:08 and 2600 lb. of ore was "fed" in at 6:38. Rapid elimination of phosphorus began as soon as the slag thinned out

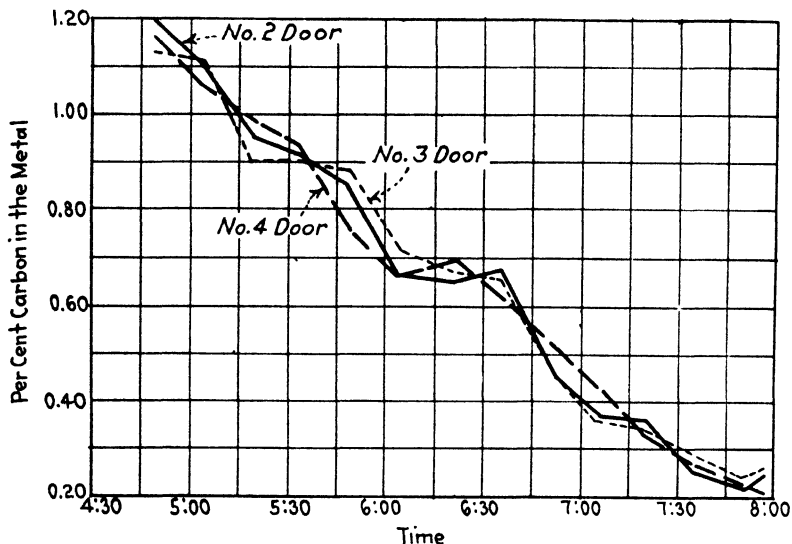


FIG. 4.—CARBON ELIMINATION DURING WORKING PERIOD.

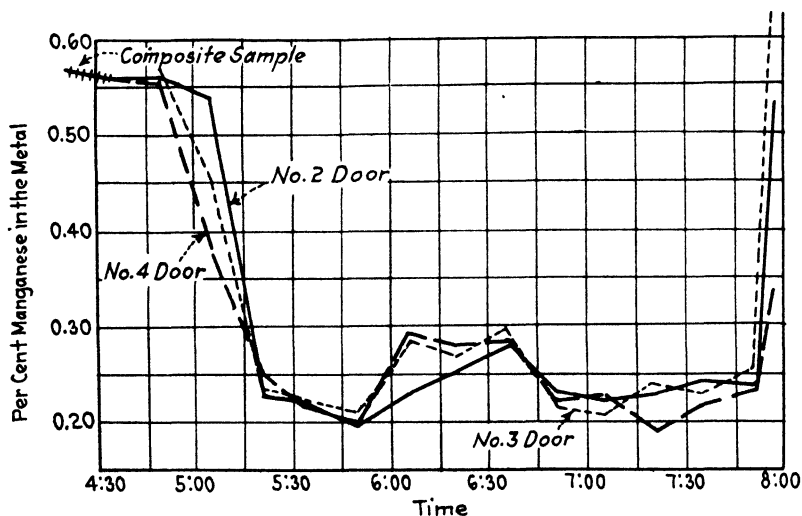


FIG. 5.—MANGANESE ELIMINATION DURING WORKING PERIOD.

after the spar addition, whereas the carbon was eliminated slowly until the ore addition, when the rate of elimination proceeded rapidly. The effect of viscosity of slag on rate of elimination is very clearly shown in the phosphorous curve, Fig. 6. The slag was still a little heavy and more

spar and ore were added at 6:58 and 7:05 respectively. The slag was now frothing somewhat and two rods were stirred through the heat to settle the frothing. The carbon was dropping at a rate of about 0.15 per cent.

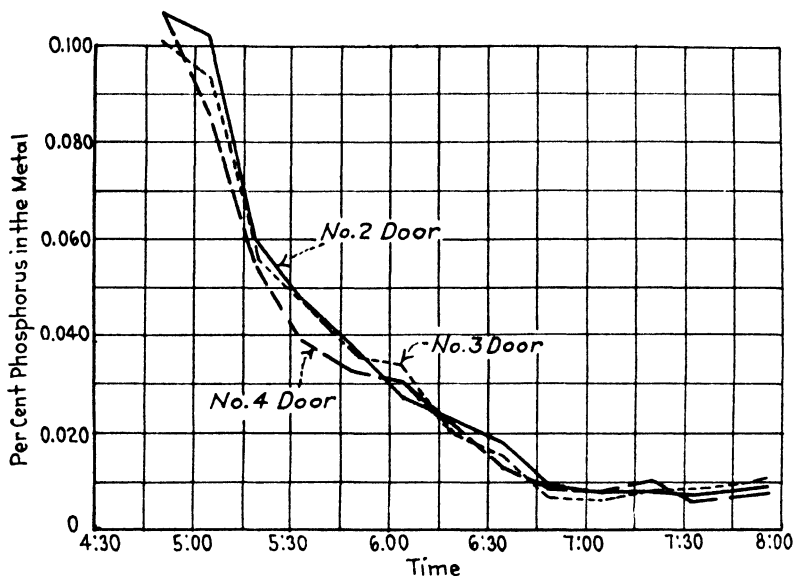


FIG. 6.—PHOSPHOROUS ELIMINATION DURING WORKING PERIOD.

per hour and the slag was of good consistency. At 7:52, 1500 lb. of ferromanganese was charged in No. 3 door. A slight foaming took place immediately after the addition. At 7:55, the metal started flowing

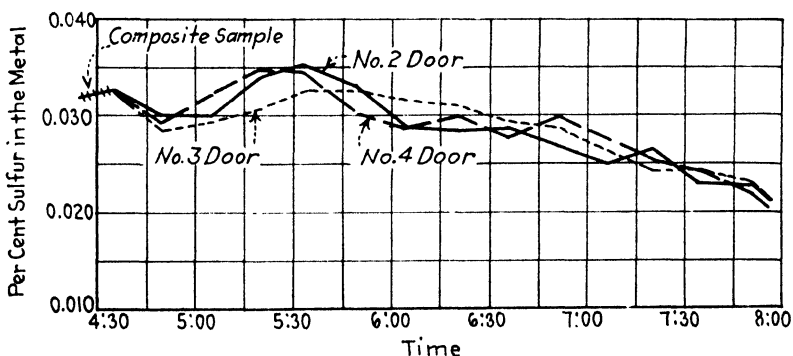


FIG. 7.—SULFUR ELIMINATION DURING WORKING PERIOD.

out of the taphole and 420 lb. of coal and 700 lb. of ferrosilicon were thrown into the ladle. The correct temperature of the metal could not be obtained because of fumes over the ladle. Two slag samples, 17244-1 and 17244-2, were taken as the slag overflowed the ladle. At 8:06 the

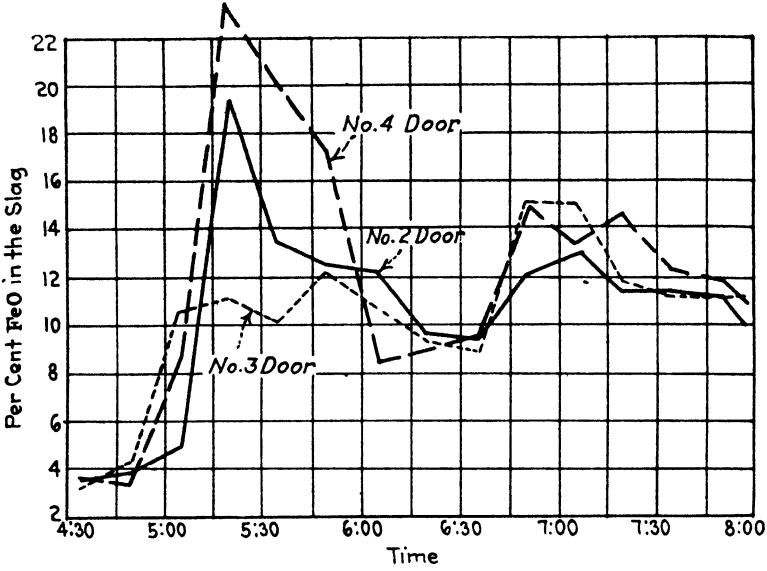


FIG. 8.—FeO IN SLAG DURING WORKING PERIOD.

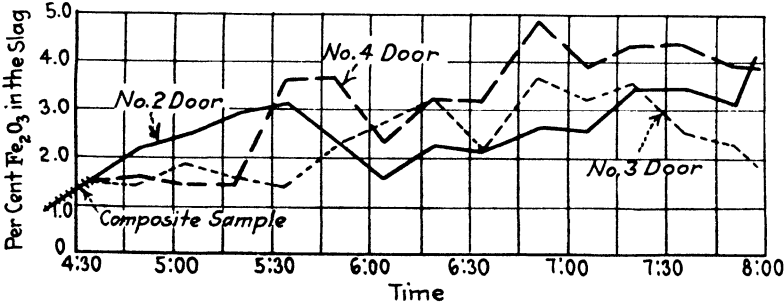


FIG. 9.—Fe₂O₃ IN SLAG DURING WORKING PERIOD.

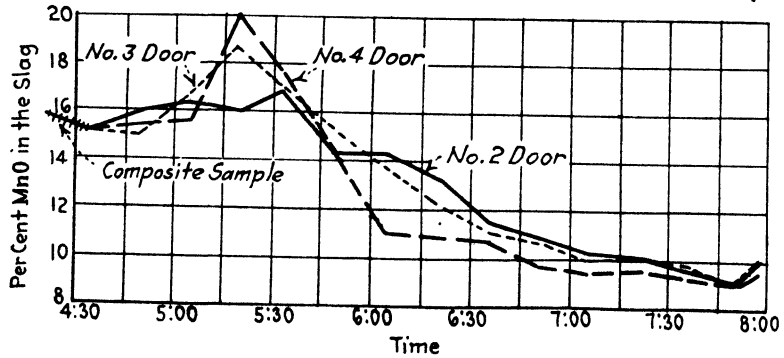


FIG. 10.—MnO IN SLAG DURING WORKING PERIOD.

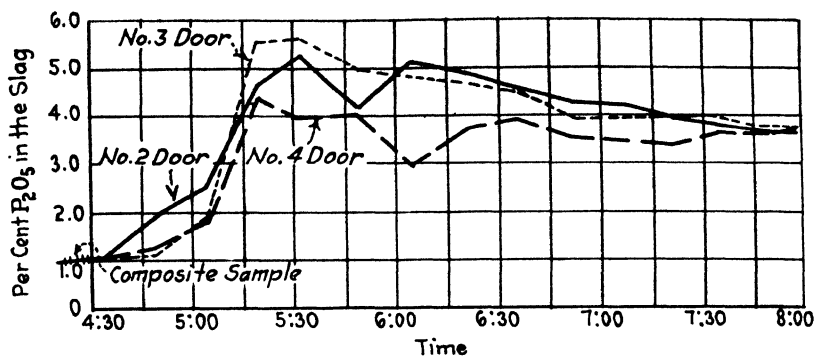
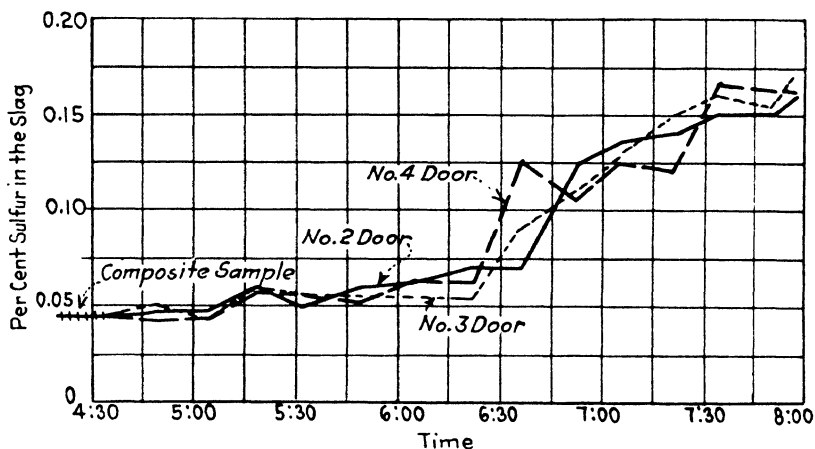
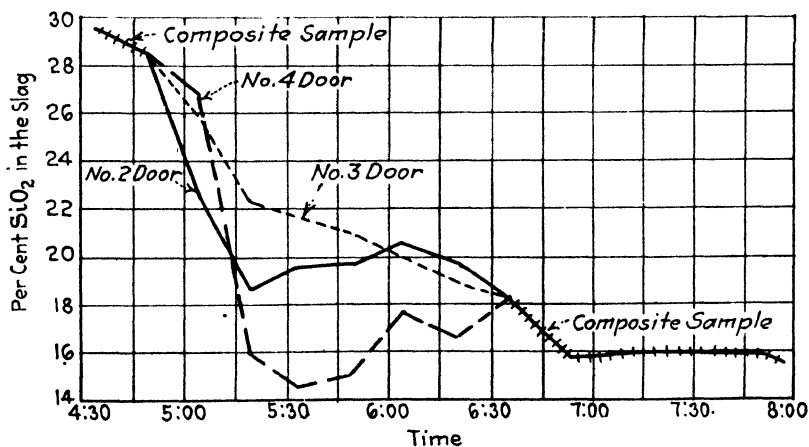
FIG. 11.— P_2O_5 IN SLAG DURING WORKING PERIOD.

FIG. 12.—SULFUR IN SLAG DURING WORKING PERIOD.

FIG. 13.— SiO_2 IN SLAG DURING WORKING PERIOD.

tap was completed and the ingots were teemed from 8:08 to 8:39. The temperature of the metal during teeming averaged 2770°F. Two slag samples, 17244-3 and 17244-4, were taken from the ladle after the last ingot had been teemed.

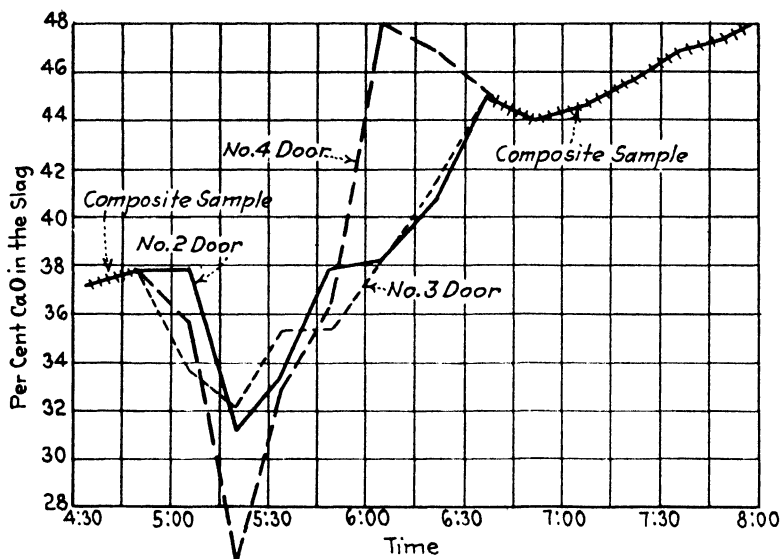


FIG. 14.—CaO IN SLAG DURING WORKING PERIOD.

RESULTS

The results are shown in Table 1 and in Figs. 1 to 18.

TABLE 1.—*Material Charged and Produced*

CHARGED	POUNDS	PRODUCTS	POUNDS
Dolomite.....	4,270	Slag.....	24,500
Limestone.....	26,000	Steel.....	248,100
Scrap.....	175,000		
Hot metal.....	80,540		
Ore.....	11,400	FINAL ANALYSIS OF STEEL	
Spar.....	716	C.....	0.372
Ferromanganese.....	1,500	Mn.....	0.608
Ferrosilicon.....	700	P.....	0.0138
Coal (ladle).....	420	S.....	0.0209
Aluminum.....	2	Si.....	0.081

DISCUSSION OF RESULTS

The greatest variation in composition during the working period is, as would be expected, immediately after the ore additions. The best illustrations of the variation are the behavior of phosphorus and manganese after the first ore addition, shown in Table 2.

TABLE 2.—*Behavior of Manganese and Phosphorus after First Ore Addition*

Time	Manganese, Per Cent.			Phosphorus, Per Cent.		
	Door 2	Door 3	Door 4	Door 2	Door 3	Door 4
4:50	0.561	0.567	0.556	0.107	0.102	0.107
5:00	3000 lb. ore in No. 4 door					
5:05	0.536	0.449	0.384	0.102	0.094	0.087
Percentage drop	4.5	20.8	31.0	4.7	7.9	18.7

Equally large variations appear in the slag composition during this period. For this reason it is absolutely necessary, in attempting to

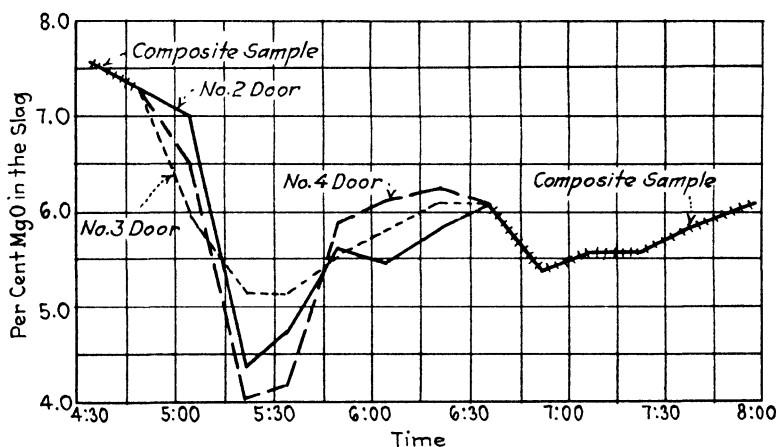


FIG. 15.—MgO IN SLAG DURING WORKING PERIOD.

determine the rate at which the various reactions proceed, to take the whole bath into consideration and not to use the middle door alone for sampling. A great many inconsistencies in the literature may be due to this consideration. Other examples of variation in composition may be seen from the diagrams given in Figs. 1 to 16.

After the first vigorous action of an ore addition has ceased, the bath begins to come to a uniform concentration as shown by sample 25. At the end of the heat the concentration of each metalloid and each slag component, with the exception of Fe_2O_3 , is uniform over the entire bath. The variation in Fe_2O_3 content at this time is undoubtedly due to the oxidizing action of the gases relative to the slag-sampling position.

The metal samples taken five minutes after the ferromanganese addition showed:

Door No. 2	0.531 per cent. Mn
Door No. 3	0.623 per cent. Mn
Door No. 4	0.336 per cent. Mn

The variations in composition were smoothed out when the metal ran into the ladle as shown in Fig. 17.

Rate of Melting Scrap

From the samples of metal and slag taken during the early lime-boil period, the amount of slag on the bath, and the amount of unmelted metal may be calculated by a silicon, manganese and phosphorus bal-

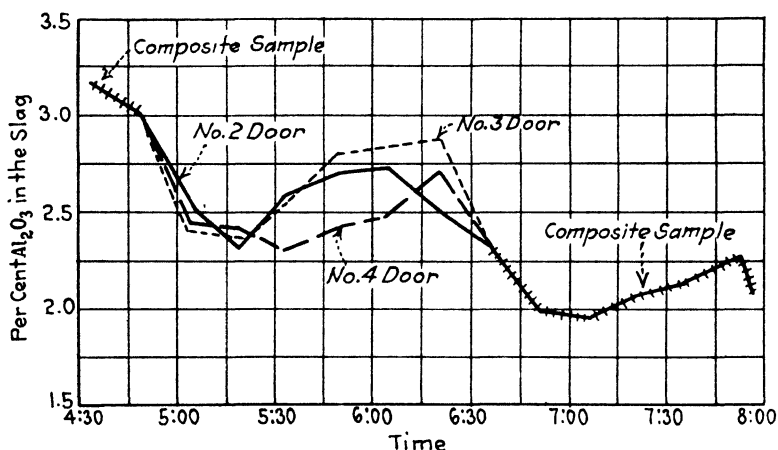


FIG. 16.— Al_2O_3 IN SLAG DURING WORKING PERIOD.

ance. The results of this calculation in reference to the melting scrap are shown in Table 3.

TABLE 3.—*Melting Scrap Data*

Sample	Time	Pounds Unmelted Scrap	Per Cent. of Scrap Melted	Time from Charging of Scrap, Hours	Time from Last Hot Metal Added, Hours
5	12:51	108,800	38	3.60	0.6
8	1:35	80,600	54	4.33	1.33
11	2:20	39,500	77	5.08	2.08
14	3:05	21,200	88	5.83	2.83

Slag Weight during Heat

The calculated slag weights at each sample are given in Table 4.

TABLE 4.—*Tabulation of Slag Weights*

SAMPLE No.	TIME	POUNDS SLAG
5	12:51	2,370
8	1:35	4,290
11	2:20	6,360
14	3:05	7,450
17	3:50	7,760
20	4:35	8,500
×21	4:50	10,160
22	5:05	11,770
23	5:20	14,230
24	5:34	15,400
25	5:50	18,500
26	6:06	19,560
27	6:21	20,600
28	6:36	21,900
29	6:51	25,600
30	7:07	26,900
31	7:21	26,800
32	7:35	27,400
33	7:52	28,300
Recorded, final		24,500

Samples 5 to 20, inclusive, are calculated on a balance of manganese, phosphorus and silicon; samples 21 to 33, inclusive, are calculated on a manganese balance. The methods give slightly different results, therefore, in calculating the erosion of the lining and the solution of the lime from the limestone, the time interval between samples 20 and 21 has been omitted.

The difference between the calculated and recorded slag weights are due to unavoidable losses of slag during and after tapping, which makes the recorded slag weight low, and to volatilization of manganese, which gives a high value for the calculated weight. The true final weight, therefore, is somewhere between the values given in the table. For the purpose of obtaining various data during the heat, the calculated slag weight will be used.

The rapid increase in slag weight between samples 5 and 11 is the result of the elimination of silicon from the metal, the erosion of the lining and the solution of lime into the slag. During the last half of the lime boil, samples 11 to 20, the increase in slag weight is small, the silicon having been eliminated and the slag being too heavy to act on the banks or dissolve the stone to any great extent. During the remainder of the heat the increase in slag weight between samples is fairly uniform except for the periods following the two ore additions, when it increases rapidly from the ore added, the action on the banks and the lime dissolved by the slag after the additions.

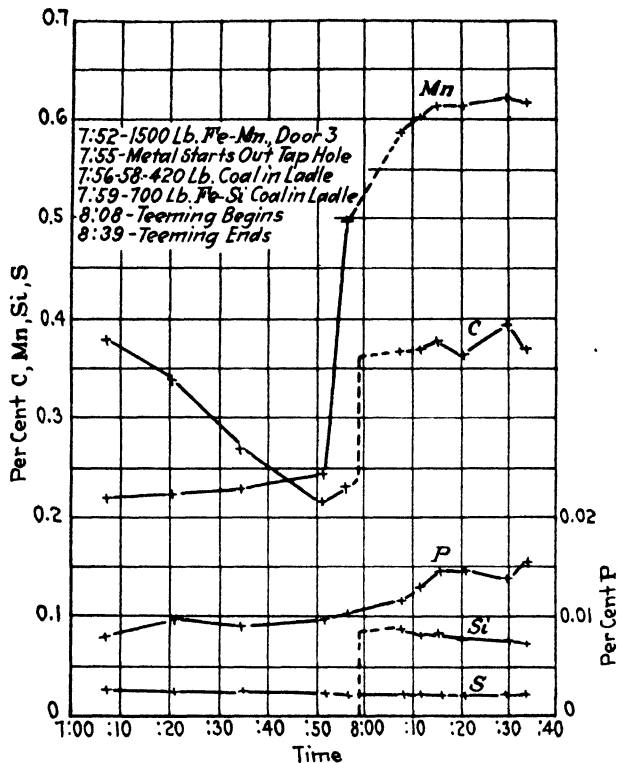


FIG. 17.—CONCENTRATION CHANGES IN INGOTS.

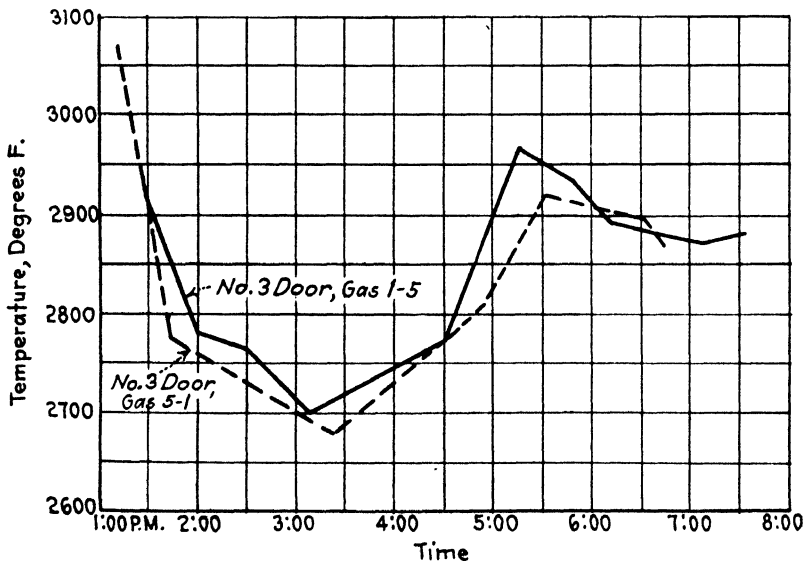


FIG. 18.—FURNACE TEMPERATURES.

Total Sulfur in the Furnace

Table 5 shows the total amount of sulfur found in the furnace during the course of the heat.

TABLE 5.—*Amount of Sulfur in Furnace during Heat*

TIME	POUNDS SULFUR
Charged—scrap and pig	105.3
In slag and metal at sample 5	101.8
In slag and metal at sample 14	84.2
In slag and metal at sample 21	77.1
In slag and metal at sample 24	92.5
In slag and metal at sample 26	83.7
In slag and metal at sample 29	98.4
In slag and metal at sample 33	100.0

During the lime boil, samples 5 to 21, a large amount of sulfur left the bath, because (1) the steam pressure and coal rate on the producers were low during part of this period and a large amount of excess air was present over the bath, which desulfurized the bath, and (2) the gases evolved from the limestone, being free from sulfur, may have desulfurized the slag.

After the steam pressure and coal rate were raised and the boiling on the lime had diminished, the bath began to pick up sulfur and continued to do so throughout the remainder of the heat except between samples 24 and 26, the drop in total sulfur in the furnace over this interval corresponding to a drop in steam pressure in the producers with a consequent increase in excess air in the furnace.

Two samples were taken from the melting scrap at 10:43 and 10:51, respectively, to obtain the effect of sulfur in the gas on the scrap at this period. The first of these was a sample of molten oxide from the surface of the scrap, the second a "wart" of metal which had "sweated out" on the surface. The oxide sample showed 0.074 per cent. S, the metal sample 0.075 per cent. S, both samples coming from scrap which analyzed 0.033 per cent. S. This showed that the scrap was absorbing sulfur from the gas, but the ratio of surface to volume of the scrap charged was so small that the total amount of sulfur absorbed was small.²

Erosion of Lining

The erosion of the lining may be readily obtained from the slag weights given in Table 4, and from the MgO content of the slag samples. The erosion of the lining depends on five factors: (1) The amount of slag in contact with the banks; (2) the acidity of the slag; (3) the temperature; (4) the viscosity of the slag; and (5) the iron oxide content of the slag.

² Some Factors Affecting the Elimination of Sulfur in the Basic Open-hearth Process. *Trans.* (1925) 71, 512.

Factor 1 may be taken into account by assuming that the surface of contact between slag and banks is proportional to the total amount of slag in the furnace.

The pounds of dolomite eroded during the course of the heat are tabulated in Table 6, the rate of erosion being expressed as pounds of lining eroded per hour per 1000 lb. of slag. The last four factors given above are listed with this rate of erosion.

TABLE 6.—*Erosion of Lining during Heat*

Time	Lining Eroded per Hour per 1000 Lb. Slag, Pounds	SiO ₂ in Slag, Per Cent.	Iron Oxides in Slag, Per Cent.	Temp. of Slag at Middle Door Degrees F.	Remarks
12:51-1:35	270	37.0	2.8	3000	
1:35-2:20	124	35.0	2.6	2800	
2:20-3:05	61	33.5	2.6	2740	
3:05-4:35	0	31.5	4.0	2730	3:20 slag begin- ning to thicken
4:35-4:50		29.0	5.2	2815	4:45 slag very viscous
4:50-5:05	24	27.0	7.7	2850	Ore at 5:00
5:05-5:50	67	18.5	20.2	2910	Ore at 5:10. 5:35 slag more fluid
5:50-6:06	44	19.0	16.5	2910	
6:06-6:21	61	19.0	14.0	2900	6:06 slag of good consistency.
					Spar at 6:09
6:21-6:36	47	18.0	13.6	2895	Spar at 6:23
6:36-6:51	37	17.0	15.7	2880	Slag a little heavy at 6:36.
					Ore at 6:40
6:51-7:07	52	16.0	17.7	2880	Spar at 6:58
7:07-7:52	27	16.0	15.6	2880	Ore at 7:05

The effect of all the factors can be seen from this table, the controlling factors being the silica content and fluidity of the slag. The erosion stops completely when the slag becomes very viscous and after each ore and spar addition, which thins out the slag, the rate of erosion increases. The most rapid rate is found when the slag is most weakly basic, the slag at the same time being very fluid.

The total amount of lining eroded during the heat was 3240 lb.

Solution of Lime from Limestone

The rate at which lime is dissolved depends on the same factors which influence the rate of erosion of the lining except that the amount of lime floating on the bath must be added, because the surface of the lime exposed to the action of the slag is a very important factor. This surface will decrease as the heat progresses and in comparing the beginning and

the end of the heat it must be taken into consideration. The mathematical treatment of this factor will not be taken up in this paper.

TABLE 7.—*Rate of Solution of Lime from Limestone*

Time	CaO per Hour from Stone in to Slag per 1000 Lb. Slag, Pounds	Iron Oxides in Slag, Per Cent.	SiO ₂ in Slag, Per Cent.	Temp. of Slag at No. 3 Door Degrees F.	Remarks
12:51-1:35	191.0	2.8	37.0	3000	
1:35-2:20	180.0	2.6	35.0	2800	
2:20-3:05	24.5	2.6	33.5	2740	
3:05-3:50	37.8	3.3	32.5	2710	3:20 slag begin- ning to thicken
3:50-4:35	25.1	4.6	30.5	2750	
4:35-4:50		5.2	29.0	2815	4:45 slag very viscous
4:50-5:05	118.0	7.7	27.0	2850	Ore at 5:00
5:05-5:20	60.0	15.3	22.0	2910	Ore at 5:10; slag more fluid at 5:35
5:20-5:34	265.0	19.1	18.7	2930	
5:34-5:50	234.0	16.9	18.5	2920	
5:50-6:06	321.0	16.5	19.0	2910	
6:06-6:21	59.5	14.0	19.0	2900	Spar at 6:09. 6:06 slag of good consistency
6:21-6:36	158.0	13.6	18.0	2895	Spar at 6:23
6:36-6:51	224.0	15.7	17.0	2880	6:36 slag a little heavy. 6:40 ore added
6:51-7:07	76.0	17.7	16.0	2880	Spar at 6:58
7:07-7:21	45.0	16.8	15.8	2880	Ore at 7:05
7:21-7:35	75.0	15.6	15.9	2880	
7:35-7:52	67.0	14.7	15.8	2880	

The amount of iron oxides in the slag and the fluidity of the slag are the controlling factors here. The fluid siliceous slags at the beginning of the heat dissolve a fairly large amount of lime but not as much as is dissolved by the highly oxidized slags of the working period. From these data the amount of limestone that had not been dissolved in the slag at the end of the heat was 3500 lb.

Comparison of Tapping Slag and Ladle Slag

	FINAL SLAG	LADLE SLAG
P ₂ O ₅	3.66	2.82
SiO ₂	15.58	23.58
FeO.....	10.70	9.64
Fe ₂ O ₃	3.28	0.93
MnO.....	9.74	10.14
CaO.....	48.00	39.60
MgO.....	6.02	5.30
S.....	0.163	0.110
Al ₂ O ₃	2.08	6.25

The slag in its attack on the ladle lining absorbed a considerable quantity of SiO_2 and Al_2O_3 , thus decreasing the basicity. The result of this decrease in basicity is rephosphorization in the metal, as shown by Fig. 17, accompanied by a marked drop in P_2O_5 in the slag; and a drop in sulfur in the slag which, however, does not show up in the metal. This may be due to the sulfur returning to the last four ingots which were not sampled.

The iron oxides, particularly Fe_2O_3 , were decreased in concentration, and the MnO was increased by oxidation of the ferromanganese added. The remaining slag components decrease in concentration because of dilution by SiO_2 and Al_2O_3 from the ladle lining.

Efficiency of Ladle Additions

The efficiency of the furnace and ladle additions is shown in Table 8.

TABLE 8.—*Efficiency of Furnace and Ladle Additions*

Material Added	Amount, Pounds	Amount Obtained in Steel, Pounds	Efficiency, Per Cent.
Carbon from coal, ferromanganese and ferro-silicon.....	497	372	75
Manganese from ferromanganese	1145	907	79
Silicon from ferrosilicon...	350	205	59

The silicon content of the steel dropped off steadily as the teeming progressed, showing that deoxidation of metal and slag by silicon continued throughout this operation. Manganese and carbon remained practically constant.

CONCLUSIONS

1. Wide variations in composition of the bath from door to door occur after ore additions. In attempting to study rate of elimination it is necessary, therefore, to sample from more than one point in the furnace.
2. The bath is of uniform composition under finishing conditions and a test from any door during this period will represent the entire bath.
3. With large amounts of excess air for combustion and with a coal analyzing 1.18 per cent. sulfur, desulfurization of the bath takes place.
4. There is a strong probability that the gas given off from the decomposition of the limestone desulfurizes the bath.
5. The erosion of the lining of the furnace is dependent, for a given amount of slag, primarily on the silica content and fluidity of the slag. During the working period the fluidity and iron oxide content of the slag are controlling factors. The effect of temperature could not be shown from the data in this paper alone.

6. The rate of solution of lime from the limestone into the slag is dependent, for a given amount of slag, on the fluidity of the slag and on its iron oxide and silica content.

7. One of the controlling factors in the rate of elimination of metalloids is the fluidity of the slag.

ACKNOWLEDGMENT

The authors wish to express their appreciation to G. W. Whitehead, who, as superintendent of the Lackawanna Steel Co., assisted in every way possible in conducting the plant test, and to Prof. R. T. Haslam, who, as director of the School of Chemical Engineering Practice, gave unfailing cooperation throughout the investigation.

TABULATION OF STEAM PRESSURE AND COAL RATE

Clock Time	Average Pressure, Pounds per Square Inch	Average Coal Rate, Pounds per Hour
8:30- 9:00 a.m.	24.0	1,625
9:00- 9:30	29.9	2,500
9:30-10:00	36.9	3,500
10:00-10:30	36.4	4,670
10:30-11:00	36.9	5,990
11:00-11:30	37.0	6,590
11:30-12:00	33.0	6,500
12:00-12:30 p.m.	27.5	6,100
12:30- 1:00	26.9	5,480
1:00- 1:30	26.5	5,130
1:30- 2:00	27.5	5,000
2:00- 2:30	17.5	4,790
2:30- 3:00	13.8	4,500
3:00- 3:30	8.9	3,850
3:30- 4:00	7.9	2,925
4:00- 4:30	11.2	2,425
4:30- 5:00	20.0	2,300
5:00- 5:30	31.5	3,125
5:30- 6:00	27.8	4,750
6:00- 6:30	20.9	5,000
6:30- 7:00	25.8	4,075
7:00- 7:30	25.0	3,730
7:30- 8:00	23.0	3,900
Total coal used on heat		50,730

ANALYSES OF METAL THROUGHOUT HEAT

Sample No.	Time	Per Cent. C	Per Cent. Mn	Per Cent. P	Per Cent. S	Per Cent. Si
A 2-2	12:05P	1.35	0.695	0.180	0.0461	0.284
2-3	12:05	2.88				
2-4	12:02	2.91				
3-2	12:22	3.21				
3-3	12:22	3.59	1.13	0.259	0.0468	0.823
4-2	12:35	2.57				
4-3	12:35	3.15				
5-2	12:51	2.36				
5-3	12:51	2.72	0.872	0.193	0.0433	0.394
6-2	1:05	2.04				
6-3	1:05	2.40				
7-2	1:20	1.75				
7-3	1:20	2.20	0.809	0.161	0.0416	0.241
7-4	1:21	2.42				
8-2	1:35	1.648				
8-3	1:35	1.768	0.770	0.152	0.0408	
8-4	1:35	1.941				
9-2	1:50	1.560				
9-3	1:50	1.583	0.735	0.136	0.0399	0.105
9-4	1:50	1.650				
10-2	2:05	1.502				
10-3	2:05	1.497	0.696	0.130	0.0380	
10-4	2:05	1.537				
11-2	2:20	1.413				
11-3	2:20	1.448	0.665	0.127	0.0364	0.0532
11-4	2:20	1.446				
12-2	2:35	1.389				
12-3	2:35	1.407	0.661	0.122	0.0353	
12-4	2:35	1.424				
13-2	2:50	1.369				
13-3	2:50	1.372	0.660	0.118	0.0343	0.018
13-4	2:50	1.368				
14-2	3:05	1.359				
14-3	3:05	1.308	0.671	0.125	0.0322	
14-4	3:05	1.310				
15-2	3:20	1.267				
15-3	3:20	1.295	0.651	0.123	0.0334	0.005
15-4	3:20	1.321				
16-2	3:35	1.266				
16-3	3:35	1.220	0.639	0.112	0.0313	
16-4	3:35	1.239				
17-2	3:50	1.277				
17-3	3:50	1.299	0.612	0.123	0.0346	
17-4	3:50	1.307				
18-2	4:05	1.218				
18-3	4:05	1.217	0.589	0.116	0.0318	
18-4	4:05	1.221				

ANALYSES OF METAL THROUGHOUT HEAT (Continued)

Sample No.	Time	Per Cent. C	Per Cent. Mn	Per Cent. P	Per Cent. S	Per Cent. Si
19-2	4:20	1.203	0.570	0.108	0.0318	
19-3	4:20	1.226				
19-4	4:20	1.226				
20-2	4:35	1.271	0.563	0.114	0.0329	
20-3	4:35	1.227				
20-4	4:35	1.202				
21-2	4:50	1.187	0.561	0.107	0.0301	Trace
21-3	4:50	1.133	0.567	0.102	0.0289	
21-4	4:50	1.165	0.556	0.107	0.0295	
22-2	5:05	1.097	0.536	0.102	0.0299	
22-3	5:05	1.113	0.449	0.0941	0.0297	
22-4	5:05	1.062	0.384	0.0870	0.0320	
23-2	5:20	0.949	0.229	0.0603	0.0342	
23-3	5:20	0.898	0.238	0.0567	0.0307	
23-4	5:20	0.983	0.248	0.0558	0.0349	
24-2	5:34	0.918	0.216	0.0480	0.0353	
24-3	5:34	0.900	0.222	0.0475	0.0327	
24-4	5:34	0.936	0.219	0.0385	0.0348	
25-2	5:50	0.848	0.201	0.0375	0.0328	
25-3	5:50	0.881	0.212	0.0362	0.0324	
25-4	5:50	0.759	0.204	0.0333	0.0299	
26-2	6:06	0.654	0.233	0.0280	0.0281	
26-3	6:06	0.720	0.288	0.0352	0.0313	
26-4	6:06	0.650	0.294	0.0317	0.0279	
27-2	6:21	0.651	0.254	0.0232	0.0283	
27-3	6:21	0.669	0.271	0.0206	0.0312	
27-4	6:21	0.685	0.274	0.0226	0.0299	
28-2	6:35	0.674	0.281	0.0188	0.0286	
28-3	6:36	0.652	0.296	0.0156	0.0295	
28-4	6:36	0.621	0.284	0.0148	0.0279	
29-2	6:51	0.454	0.228	0.0092	0.0266	
29-3	6:51	0.455	0.216	0.0074	0.0290	
29-4	6:51	0.506	0.221	0.0089	0.0293	
30-2	7:07	0.365	0.224	0.0083	0.0250	Trace
30-3	7:07	0.356	0.207	0.0071	0.0265	
30-4	7:07	0.425	0.228	0.0082	0.0272	
31-2	7:21	0.358	0.231	0.0092	0.0260	
31-3	7:21	0.337	0.240	0.0092	0.0242	
31-4	7:21	0.332	0.195	0.0107	0.0251	
32-2	7:35	0.255	0.243	0.0094	0.0229	
32-3	7:35	0.281	0.227	0.0096	0.0245	
32-4	7:35	0.267	0.219	0.0076	0.0246	
33-2	7:52	0.208	0.239	0.0095	0.0229	
33-3	7:52	0.235	0.253	0.0104	0.0232	
33-4	7:52	0.224	0.235	0.0088	0.0222	
34-2	7:57	0.237	0.531	0.0106	0.0208	Trace
34-3	7:57	0.256	0.623	0.0123	0.0208	
34-4	7:57	0.201	0.336	0.0084	0.0201	

ANALYSES OF SLAG THROUGHOUT HEAT (Continued)

Sample No.	Time	Per Cent. FeO	Per Cent. FeO ₂	Per Cent. MnO	Per Cent. FeO ₂	Per Cent. S
19-2	4:20	3.24	0.98	15.86	1.01	0.0449
19-3	4:20	3.77				
19-4	4:20	3.62				
20-2	4:35	3.49	1.49	15.22	1.11	0.0445
20-3	4:35	3.29				
20-4	4:35	3.60				
21-2	4:50	3.92	2.17	15.85	1.94	0.0472
21-3	4:50	4.35	1.40	15.13	1.17	0.0485
21-4	4:50	3.40	1.58	15.34	1.23	0.0454
22-2	5:05	4.99	2.46	16.40	2.49	0.0497
22-3	5:05	10.54	1.85	16.62	1.88	0.0433
22-4	5:05	8.69	1.44	15.54	1.87	0.0471
23-2	5:20	19.45	2.86	15.96	4.67	0.0595
23-3	5:20	11.13	1.57	18.66	5.55	0.0574
23-4	5:20	23.23	3.49	19.97	4.34	0.0600
24-2	5:34	13.35	3.12	16.82	5.22	0.0518
24-3	5:34	10.02	1.35	17.19	5.61	0.0568
24-4	5:34	20.07	3.58	17.61	3.97	0.0566
25-2	5:50	12.37	2.37	14.21	4.22	0.0578
25-3	5:50	12.18	2.24	15.16	4.95	0.0540
25-4	5:50	17.27	3.66	14.24	4.05	0.0507
26-2	6:06	12.20	1.53	14.30	5.11	0.0626
26-3			No sample			
26-4	6:06	8.46	2.27	11.13	2.95	0.0630
27-2	6:21	9.53	2.24	13.30	4.90	0.0703
27-3	6:21	9.30	3.24	12.26	4.68	0.0534
27-4	6:21	8.99	3.11	10.80	3.69	0.0622
28-2	6:36	9.39	2.11	11.47	4.52	0.0700
28-3	6:36	8.79	2.16	11.13	4.45	0.0888
28-4	6:36	9.48	3.15	10.74	3.84	0.1267
29-2	6:51	12.07	2.64	10.75	4.22	0.1225
29-3	6:51	15.10	3.67	10.54	3.90	0.1113
29-4	6:51	15.05	4.82	9.69	3.51	0.1060
30-2	7:07	12.86	2.56	10.19	4.19	0.1390
30-3	7:07	14.99	3.22	9.96	3.89	0.1298
30-4	7:07	13.36	3.90	9.40	3.47	0.1268
31-2	7:21	11.26	3.40	10.07	3.88	0.1399
31-3	7:21	11.81	3.52	10.02	3.92	0.1483
31-4	7:21	14.48	4.35	9.50	3.33	0.1220
32-2	7:35	11.25	3.46	9.63	3.78	0.1517
32-3	7:35	11.07	2.57	9.70	3.89	0.1578
32-4	7:35	12.18	4.43	9.30	3.61	0.1660
33-2	7:52	11.13	3.14	9.17	3.67	0.1522
33-3	7:52	11.12	2.30	9.13	3.71	0.1529
33-4	7:52	11.76	3.93	9.03	3.63	0.1622
34-2	7:57	9.99	4.09	9.95	3.71	0.1578
34-3	7:57	11.10	1.89	9.93	3.67	0.1598
34-4	7:57	11.02	3.85	9.34	3.59	0.1620

ANALYSES OF SLAG THROUGHOUT HEAT (Continued)

Sample No.	Time	Per Cent. SiO ₂	Per Cent. CaO	Per Cent. MgO	Per Cent. Al ₂ O ₃
A 1-3	11:42A				
2-2			No sample		
2-3	12:05	19.46	40.50	3.65	2.50
2-4	12:02				
3-2					
3-3			Not analyzed		
4-2			do		
4-3			do		
5-2	12:51	37.50	33.62	4.85	4.17
5-3	12:51				
6-2					
6-3			Not analyzed		
7-2			do		
7-3			do		
7-4			do		
8-2	1:35	35.80	39.20	8.04	3.93
8-3	1:35				
8-4	1:35				
9-2			Not analyzed		
9-3			do		
9-4			do		
10-2			do		
10-3			do		
10-4			do		
11-2	2:20	33.80	38.72	8.35	3.42
11-3	2:20				
11-4	2:20				
12-2			Not analyzed		
12-3			do		
12-4			do		
13-2			do		
13-3			do		
13-4			do		
14-2	3:05	33.35	38.30	8.66	3.45
14-3	3:05				
14-4	3:05				
15-2			Not analyzed		
15-3			do		
15-4			do		
16-2			do		
16-3			do		
16-4			do		
17-2	3:50	31.95	38.72	7.74	3.60
17-3	3:50				
17-4	3:50				
18-2			Not analyzed		
18-3			do		
18-4			do		

ANALYSES OF SLAG THROUGHOUT HEAT (Continued)

Sample No.	Time	Per Cent. SiO ₂	Per Cent. CaO	Per Cent. MgO	Per Cent. Al ₂ O ₃
19-2			do		
19-3			do		
19-4			do		
20-2	4:35	29.51	37.72	7.54	3.16
20-3	4:35				
20-4	4:35				
21-2	4:50	28.48	37.90	7.28	2.99
21-3	4:50				
21-4	4:50				
22-2	5:05	22.50	37.85	6.99	2.52
22-3	5:05	25.92	33.93	5.98	2.40
22-4	5:05	27.00	35.67	6.49	2.44
23-2	5:20	18.62	30.80	4.35	2.32
23-3	5:20	22.30	32.20	5.15	2.36
23-4	5:20	15.90	25.80	4.03	2.40
24-2	5:34	19.58	33.55	4.77	2.58
24-3	5:34	21.73	35.50	5.12	2.55
24-4	5:34	14.41	33.13	4.15	2.30
25-2	5:50	19.65	37.92	5.60	2.70
25-3	5:50	21.00	35.57	5.53	2.80
25-4	5:50	15.00	36.50	5.89	2.41
26-2	6:06	20.47	38.35	5.45	2.73
26-3			No sample		
26-4	6:06	17.74	48.14	6.13	2.47
27-2	6:21	19.76	40.75	5.81	2.50
27-3	6:21	18.82	41.90	6.10	2.87
27-4	6:21	16.56	47.05	6.24	2.70
28-2	6:36	18.20	45.14	6.07	2.34
28-3	6:36				
28-4	6:36				
29-2	6:51	15.70	44.00	5.36	1.98
29-3	6:51				
29-4	6:51				
30-2	7:07	15.77	44.60	5.58	1.94
30-3	7:07				
30-4	7:07				
31-2	7:21	15.91	45.65	5.52	2.07
31-3	7:21				
31-4	7:21				
32-2	7:35	15.85	46.90	5.78	2.14
32-3	7:35				
32-4	7:35				
33-2	7:52	15.86	47.65	6.00	2.26
33-3	7:52				
33-4	7:52				
34-2	7:57	15.58	48.00	6.02	2.08
34-3	7:57				
34-4	7:57				

ANALYSES OF SLAG THROUGHOUT HEAT (Continued)

Sample No.	Time	Per Cent. FeO	Per Cent. Fe ₂ O ₃	Per Cent. MnO	Per Cent. P ₂ O ₅	Per Cent. S
17244-1	8:04 P	9.65	4.01	10.25	3.45	0.1405
17244-2	8:04	9.25	5.00	10.27	3.39	0.1405
17244-3	8:39	9.84	0.60	10.26	2.84	0.1045
17244-4	8:39	9.44	1.26	10.01	2.79	0.1150
			Per Cent. SiO ₂	Per Cent. CaO	Per Cent. MgO	Per Cent. Al ₂ O ₃
17244-1 } 17244-2 } 17244-3 } 17244-4 }			16.55	46.55	5.93	2.20
			23.58	39.60	5.30	6.25

SPECIAL SAMPLES

SAMPLE No.	TIME	PER CENT. FeO	PER CENT. Fe ₂ O ₃	PER CENT. MnO	PER CENT. P ₂ O ₅	PER CENT. S
AX 1-3	10:43 A			1.54		0.074
AX 3-4	6:11 P	11.05	1.93	11.19	3.89	0.0526
PER CENT. SiO ₂		PER CENT. CaO		PER CENT. MgO		PER CENT. Al ₂ O ₃
16.83		42.50		8.13		2.39

RAW MATERIALS

Pig Iron (composite sample)

PER CENT. C	PER CENT. MN	PER CENT. P	PER CENT. S	PER CENT. Si
4.14	1.37	0.362	0.059	1.17

Scrap (average analysis)

PER CENT. C	PER CENT. MN	PER CENT. P	PER CENT. S	PER CENT. Si
0.67	0.84	0.025	0.033	0.149

Ferromanganese

PER CENT. C	PER CENT. MN	PER CENT. P	PER CENT. Si
6.44	76.4	0.25	0.86

Ferrosilicon

PER CENT. C	PER CENT. P
0.337	0.04

Coal for Producers—1.18 Per Cent. S

Sample	Stone	Dolomite	Ore
Manganese oxide (MnO).....	0.083	0.014	0.09
Silica (SiO ₂).....	1.55	0.60	5.37
Total iron as Fe ₂ O ₃	0.47	0.85	75.31
Alumina (Al ₂ O ₃).....	0.14	0.20	1.66
Total sulfur (S).....	none	none	none
Calcium oxide (CaO).....	52.35	54.69	not determined
Magnesium oxide (MgO).....	1.90	37.22	not determined
Phosphorus pentoxide (P ₂ O ₅).....	trace	trace	2.20
Moisture.....	0.38	none	not determined
Loss on ignition less moisture	43.24	6.68	not determined

Chemical Equilibrium of Manganese, Carbon, and Phosphorus in the Basic Open-hearth Process

BY C. H. HERTY, JR.,* LACKAWANNA, N. Y.

(New York Meeting, February, 1926)

The results of a study of the open-hearth process from the physicochemical viewpoint are given. This study includes experimentation in small laboratory furnaces and in standard 100-ton furnaces. The behavior of manganese, carbon and phosphorus are quantitatively explained. The action of "residual" manganese is discussed with reference to its relation to iron oxide dissolved in the metal. The solubility of CO in steel and its relation to dissolved FeO and carbon is given. The equation for phosphorus elimination has been tested out on a 200-ton furnace and the results are given in the text.

THE effect of temperature and slag composition on the elimination of metalloids in the basic open-hearth process has been qualitatively understood since the early days of steel making. The quantitative effect has, however, only recently been brought to attention. The effect of slag composition has received more attention than that of temperature, primarily because the range of finishing temperatures in the basic open-hearth process is small compared to the large variations found in the composition of the slag at different periods during the process, and to the variations occurring with the use of raw materials of different degrees of impurity.

The effect of slag composition on the elimination of metalloids has been studied by Styri¹ from the thermochemical standpoint. This method is open to serious errors, in that thermochemical data at 2900° F. are very inaccurate and in many cases completely lacking. Feild² has calculated equilibrium constants from the rate at which the metalloids are eliminated. The effect of slag viscosity on rate of elimination will affect the constants calculated by this method. Whitely,³ Colcough⁴ and others have used slag compositions as the basis for calculation of constants by which the extent of elimination may be calculated.

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¹ *Jnl. Iron and Steel Inst.* (No. 2, 1923) 189.

² *Trans. Faraday Soc.* (1925) 21.

³ *Cleveland Inst. of Engrs.* (Dec., 1922).

⁴ *Jnl. Iron and Steel Inst.* (No. 1, 1924).

The object of this paper is to present experimental data from both laboratory furnaces and full-scale equipment from which the equilibrium conditions between slag and metal and in the metal itself are determined for some of the reactions which occur in the basic open-hearth process. The application of these equilibrium conditions to the effect of temperature and quality of raw materials charged to the furnace is shown.

Three basic principles of physical chemistry are taken into consideration in this work: (1) the law of mass action; (2) the Van't Hoff isochore; and (3) the distribution law.

THE LAW OF MASS ACTION

For any reversible reaction of the type $nA + mB = oC + pD$ the law of mass action states that the rate of reaction is proportional to the active concentration of each component and that at equilibrium the rate of reaction between A and B is just balanced by the rate of reaction between C and D , the net result being a constant concentration of each of the reactants in the system under consideration. This is expressed mathematically as

$$K = \frac{(C)^o (D)^p}{(A)^n (B)^m}$$

Since concentration alone is involved, the quantity of material present need not be taken into consideration.

THE VAN'T HOFF ISOCHORE

The Van't Hoff isochore is the quantitative statement of the Le Chateleur-Braun principle which states that if a system be in equilibrium and one of the conditions, such as temperature, be altered, the system will change in such a direction as to oppose the change in temperature. If a reaction evolves heat, it will be favored by a low temperature, while if it absorbs heat it will be favored by a high temperature. The Van't Hoff isochore is mathematically stated as

$$\frac{d \log K}{dt} = \frac{Q}{RT^2},$$

where K is the mass action equilibrium constant, T the absolute temperature, Q the heat absorbed, and R the gas constant per mol. If Q is assumed to be constant over the temperature range found in open-hearth operation, the reaction may be integrated between the temperature T and T_1 ($T_1 > T$),

$$\log_e \frac{K_1}{K} = \frac{Q}{R} \left(\frac{1}{T} - \frac{1}{T_1} \right), \quad (A)$$

and by the equation we may calculate the equilibrium constant at any temperature if the heat of reaction and the constant at any other temperature are known, or from the equilibrium constants at two temperatures we may calculate the heat of reaction.

THE DISTRIBUTION LAW

The distribution law of Nernst⁶ may be briefly stated as follows: If a substance be dissolved in two immiscible or slightly miscible liquids, it possesses a constant distribution coefficient at a given temperature when it has the same molecular weight in both solvents.

EXPERIMENTAL PROCEDURE

The experimental work⁶ was carried out in laboratory furnaces of $\frac{1}{2}$ lb. capacity and in standard 100-ton stationary open hearths. A carbon resistance furnace was used for the laboratory experiments, zirconia and magnesia crucibles were used; zirconia when no silicate or phosphate slag was present, magnesia when these slags were present. Zirconia was rapidly eroded by these slags. Electrolytic iron containing 0.03 per cent. carbon, 0.44 per cent. oxygen, and free from sulfur, phosphorus, and manganese, was used in the experimental work. The other materials were prepared in the laboratory or obtained in as pure a state as possible from commercial laboratories.

The plant data were obtained in the furnaces of the Lackawanna Plant of the Bethlehem Steel Co.

REACTIONS OF ELIMINATION

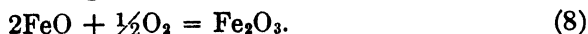
The reactions to be considered are:

1. $\text{Mn} + \text{FeO} = \text{MnO} + \text{Fe}$ (FeO in metal)
2. $\text{Mn} + \text{FeO} = \text{MnO} + \text{Fe}$ (FeO in slag)
3. $x\text{MnO} + \text{SiO}_2 = x\text{MnO} \cdot \text{SiO}_2$
4. $\text{C} + \text{FeO} = \text{CO} + \text{Fe}$ (FeO in metal)
5. $\text{C} + \text{FeO} = \text{CO} + \text{Fe}$ (FeO in slag)
6. $2\text{P} + 8\text{FeO} = 3\text{FeO} \cdot \text{P}_2\text{O}_5 + 5\text{Fe}$ (FeO in slag)
7. $2\text{P} + 5\text{FeO} + 3\text{CaO} = \text{CaO} \cdot \text{P}_2\text{O}_5 + 5\text{Fe}$ (FeO in slag)

Neglecting temporarily the effect of temperatures, one of two factors or both can be found in all the reactions; namely, iron oxide and basicity of the slag. Before considering the separate reactions it will be necessary to define the concentration of iron oxide and available base in the slag.

IRON OXIDE IN THE SLAG

The two iron oxides FeO and Fe_2O_3 are almost always found in basic open-hearth slags and the action of these two oxides has been often discussed. The Fe_2O_3 is formed by the action of the oxidizing gases above the bath on the FeO in the slag:



⁶ *Zeit. Phys. Chem.* (1891) 8, 110.

⁶ C. H. Herty, Jr.: Doctor's Thesis, Mass. Inst. Tech., 1924.

The Fe_2O_3 is carried to the slag-metal surface either by diffusion or convection and it is there either reduced to FeO by the reaction



or is reduced by carbon, partly or completely.



At the temperatures of open-hearth steel making it is highly improbable that Fe_2O_3 can exist in contact with iron without being reduced to FeO . Normal slag-sampling methods give only the upper layer of slag which is in contact with the furnace gases and give no insight into conditions at the slag-metal surface. However, the following conditions are always found in the slag samples during certain periods of a heat:

1. When good agitation is taking place in the bath the ratio $\frac{\text{Fe}_2\text{O}_3}{\text{FeO}}$ is usually low. The Fe_2O_3 in a slag immediately after an ore addition is excluded from this statement, of course, since Fe_2O_3 is added to the slag at that time.

2. When a heat is "dead" either with high or low carbon the ratio $\frac{\text{Fe}_2\text{O}_3}{\text{FeO}}$ in the slag is always high compared to that with a similar carbon content when the bath is working well. This condition is shown in Table 1.

TABLE 1.—*Comparison of Dead Heat and Good Bath*

Heat	Condition	Metal, Per Cent. C	Slag, Per Cent. FeO	Slag, Per Cent. Fe ₂ O ₃	Ratio Fe ₂ O ₃ /FeO
S	Melted "dead".....	0.11	7.49	9.50	1.27
M	Working.....	0.13	12.56	4.73	0.38
N	Working.....	0.12	12.34	7.13	0.58
Q	Working.....	0.13	8.49	3.64	0.43

Von Juptner⁷ says "A special class of oxide slags occur in iron alloys under certain conditions in the form of inclusions. Their characteristic is the deficiency of sesquioxides. This is owing to the fact they are at once reduced to monoxides by the excess of the metal near them." The same condition should hold at the slag-metal surface.

For the determination of equilibrium conditions at the slag-metal surface, therefore, it will be assumed that the Fe_2O_3 found in slags is reduced by iron to FeO by equation (9), one molecule of Fe_2O_3 yielding

⁷ *Jnl. Iron and Steel Inst.* (No. 2, 1900).

three molecules of FeO . Thus a slag containing 10 per cent. FeO and 5 per cent. Fe_2O_3 would be considered as containing

$$(10 + (5) \frac{(3\text{FeO})}{(\text{Fe}_2\text{O}_3)}) = 10 + 5 \frac{(215.4)}{(159.7)} = 16.8 \text{ per cent. FeO.}$$

Furthermore, all the FeO in the slag will be considered as available for reaction with the metalloids.

AVAILABLE BASE IN THE SLAG

The actual concentration of the lime cannot be taken, as some of it is already in use in the neutralization of the P_2O_5 and SiO_2 in the slag, and since the actual compounds formed in the slag are not known, resort must be made to some empirical formula for "free lime" or "available base."

Whitely⁸ has calculated the "basicity index" of a number of slags by the formula:

$$\text{Basicity index} = \frac{\text{Total mols bases} - 3 \times \text{mols } \text{P}_2\text{O}_5}{\text{Mols } \text{SiO}_2}$$

Richarme⁹ calculated the "acidity" of the slag for one heat by a more complicated method and Wilson¹⁰ and others have used the "acid" or "basic" oxygen as a standard for slags.

The compounds formed in slags are exceedingly complicated and comparatively little is known of their actual composition. Open-hearth slags are generally considered silicate slags containing dissolved phosphates and sulfides, the silicates being binary, ternary, or possibly compounds of even higher types. These silicates may be of almost any composition, as lime and silica, for instance, combine in any proportions, and as ternary compounds of the components in slags are commonly known. The slag, therefore, may have all its components combined and yet be either acid or basic, depending on the relative amounts of the components.

Experience has shown that if two compounds are considered, the first containing more base per unit of acid than the second, the *activity* or *escaping tendency* of the first (as defined by G. N. Lewis¹¹) as a basic component will be the greater. The basicity of a slag, therefore, may be expressed as the excess base above that required to satisfy the acids, the basis of the acid-base compounds being those which appear to be the most neutral in their character. The expression for "available lime" "basicity index" or whatever name may be given should be a concentration term, because its concentration affects the equilibrium.

We will assume, for the purpose of calculating the "available lime," that the neutral compounds in the slag are $3\text{CaO} \cdot \text{P}_2\text{O}_5$, $\text{CaO} \cdot \text{SiO}_2$, $\text{MgO} \cdot \text{SiO}_2$, $2\text{FeO} \cdot \text{SiO}_2$, $3\text{MnO} \cdot \text{SiO}_2$. The Al_2O_3 and Fe_2O_3 are considered

⁸ *Op. cit.*

⁹ *Rev. Metal. Mem.* (1910) 993.

¹⁰ *Jnl. Iron and Steel Inst.* (No. 1, 1920), 265.

¹¹ Lewis and Randall: "Applied Thermodynamics," 176.

as neutral and, with the sulfur, are usually small enough to be neglected. FeO and MnO are considered less basic than lime, MnO being the weaker. Because of lack of data concerning the basicity of these oxides relative to lime, they are arbitrarily given the values of 2 and 3.

Von Juptner¹² says, "It may at once be admitted that the silica shows greater combining power for lime than for ferrous oxide, manganese oxide, alumina, etc., but in accordance with the law of masses, it is certain that in the presence of all these bases, silica must be combined not only with the lime but with all these bases, in accordance on one hand with the relative degrees of affinity and on the other with the mass ratios."

The available base will be expressed as "mols available base per 100-wt. units of slag," and will be designated in the text as A. B. A calculation of available base is given in Table 2.

To obtain the number of mols of each component in the slag the percentage of each component is divided by its molecular weight. From the mols of each component and from the compounds listed above, the available base is calculated as shown in Table 2.

TABLE 2.—*Calculation of Available Base*

Basis: 100-wt. Units of Slag

Weight Per Cent. ÷ Mol. Weight = Mols. per 100-wt. Units

Substances	Weight, Per Cent.	Mol. Weight	Mols per 100- wt. Units
SiO ₂	21.86	60.3	0.363
P ₂ O ₅	3.21	142.2	0.023
FeO.....	13.37	71.8	0.186
MnO.....	6.25	70.9	0.088
CaO.....	43.97	56.0	0.784
MgO.....	7.44	40.3	0.184

BASES	
CaO	0.784
MgO	0.184
FeO	
$\frac{2}{}$	= 0.093
MnO	
$\frac{3}{}$	= 0.027

ACIDS	
SiO ₂	= 0.363
P ₂ O ₅ × 3	= 0.069

Total acids 0.432

Total bases 1.088

Total bases — total acids = 1.088 — 0.432 = 0.656 mol available base per 100-wt. units of slag.

EQUILIBRIUM CONDITIONS

In order that the slag and metal may be in equilibrium with regard to any metalloid, it is necessary (1) that the composition of the metal and slag be constant with respect to the metalloid in question or any of the constituents which affect its elimination; (2) that the slag be sufficiently

¹² Von Juptner: *Op. cit.*

fluid and that there be enough action on the bath to ensure against a "false" equilibrium. This condition of false equilibrium is often reached if the slag becomes so viscous that interaction between slag and metal is completely stopped. When the slag "opens up" after such a condition, the metalloids will either be eliminated from the metal or will return to it, depending on the composition of the slag. A typical example of false equilibrium is found in the condition at the end of the lime boil in heat B, shown in Table 3.

TABLE 3.—*Typical Example of False Equilibrium*

Time	Per Cent. C	Per Cent. FeO in Slag	Per Cent. Fe ₂ O ₃ in Slag	Condition of slag
4:00	1.40	4.31	0.59	thin
4:30	1.13	3.09	0.28	thin
5:00	1.07	3.17	0.12	thin
5:30	1.04	3.45	0.94	very heavy slag
5:40		800 lb. spar added		
6:02	0.83	4.75	1.27	slag thin
6:23	0.73	4.92	1.17	slag thickening

As the slag thickens, the reaction practically stops in spite of an increase in iron oxide in the slag, and as soon as the slag is thinned out, the elimination of carbon proceeds very rapidly. In all the experimental work the question of false equilibrium has been very carefully held in mind. In attempting to check the experimental results by data from other sources, the absence of data on slag conditions often causes apparent inconsistencies in the results.

NOMENCLATURE

All slag concentrations except when otherwise stated are expressed in "mols per 100-wt. units." This is obtained by dividing the weight per cent. of any constituent by its molecular weight.

All metal concentrations are expressed as per cent. by weight. This simplifies the visualization of the final results and the application of these results. The change from weight per cent. to mol per cent. changes the constants for any reaction by a constant ratio.

The constants for the different metalloids are expressed as follows: Carbon, K_c ; manganese, K_M ; phosphorus, K_p .

Heat A has been given twice the weight of any other heat in calculating the constants, on account of the precision of sampling on this heat.

MANGANESE

The reactions by which manganese is eliminated are:

- (1) $\text{Mn} + \text{FeO} = \text{MnO} + \text{Fe} + \text{heat.}$ (FeO and MnO in metal.)
- (2) $\text{Mn} + \text{FeO} = \text{MnO} + \text{Fe} + \text{heat.}$ (FeO and MnO in slag.)

The equilibrium constants for these reactions are:

$$(1) \quad K_{Mn} = \frac{(\text{MnO})_{\text{metal}}}{(\text{Mn})(\text{FeO})_{\text{metal}}} \quad (E)$$

$$(2) \quad K'_{Mn} = \frac{(\text{MnO})_{\text{slag}}}{(\text{Mn})(\text{FeO})_{\text{slag}}} \quad (C)$$

The Fe on the right hand side of the equations is neglected, since it is the solvent. Equation (C) enables us to determine the equilibrium conditions in the metal if the concentrations of MnO and FeO in the metal are assumed, in accordance with the distribution law, to be proportional to the concentrations of MnO and FeO in the slag. Equation (3) involves the dissociated acids in the slag and will be considered later.

Since there are no data on the solubility of MnO in the metal, except that it is very sparingly soluble, it will be assumed, as above, that its concentration is proportional to the concentration of MnO in the slag, and since its solubility is small we may neglect it in computing the manganese concentration in the metal. Furthermore, since the amount of manganese sulfide is probably smaller than the amount of iron sulfide, *in the furnace*, the manganese in combination with sulfur may be neglected. Investigational work on this point is being carried out.

By these two assumptions we may use the total manganese in the metal in the equilibrium constants for the reactions given above.

Other conditions being equal, the more basic a slag, the more manganese there will be found in the metal, since the CaO will displace MnO from its combination with silica and P_2O_5 . Furthermore, since the reactions are exothermic, the higher the temperature the further the reaction will go to the left and the greater will be the amount of manganese in the metal. An increase in either basicity or temperature will therefore lower the numerical value of K . The effect of varying ratios of SiO_2 to P_2O_5 in the slag will also affect the numerical value of K if either one is more easily reducible by iron than the other.

Neglecting temporarily the effect of ratio of silica to P_2O_5 in the slag the constant K'_{Mn} may be expressed as follows. For a given temperature and a given basicity of slag, the manganese in the metal will be constant when the MnO and the FeO in the slag are constant. If either temperature or basicity change, the amount of manganese in the metal will change according to the degree in which these factors affect the numerical value of the constant.

Laboratory Experiments

In the experimental work in the laboratory furnaces electrolytic iron was melted in zirconia crucibles and a known amount of MnO_2 added to the iron. After the metal and slag, which was composed of FeO and MnO only, had been molten for about $\frac{1}{2}$ hr., the metal was cast into small test pieces. It was impossible to obtain samples of the slag on account of the

small amount present, and its composition has been calculated from the amount of materials charged and the analysis of the iron. The results are shown in Table 4.

The high amounts of FeO found in the metal suggest that the recorded temperatures are somewhat low. The three runs were all made within an hour of each other in the same furnace and it is probable that the temperature 2840 is closest to the true temperature, the others being somewhat lower but not as low as is shown in Table 4. The constant K'_{Mn} for these three runs is, respectively, 3.5, 5.4 and 7.5, where MnO and FeO are expressed as mols per 100-wt. units and Mn is expressed as weight per cent.

TABLE 4.—*Composition of Slag*

Run No.	Metal		Slag (Calc.)		Temp., Degrees F.
	Per Cent. Mn	Per Cent. FeO	Per Cent. MnO	Per Cent. FeO	
1	0.019	1.51	6.2	93.8	2840
2	0.046	1.66	19.6	80.4	2695
3	0.053	1.31	28.5	71.5	2670

It has been shown that rising temperature should cause the reaction to go to the left and the constant to decrease, as is the case in the experimental runs. The quantitative effect of temperature can scarcely be shown here, because of the doubtful accuracy of the temperatures recorded.

Plant Study

In comparing results obtained in full-scale furnaces (100 tons) with the experimental work, it must be remembered that in addition to the reaction of iron oxide with manganese there is the secondary reaction of the manganese oxide combining with the acid components of the slag. In Table 5 the basicity of the slag, as calculated previously, is listed with the constant calculated for the fundamental reaction of elimination.

TABLE 5.—*Equilibrium under Finishing Conditions*

Heat	Sample	K'	Temp., Degrees F.	Available Base
<i>C</i>	19	3.09	2840	0.684
<i>P</i>		2.90	2895	0.737
<i>K</i>		2.80	2915	0.786
<i>Q</i>		2.57	2905	0.779
<i>A*</i>	33	2.48	2895	0.770
<i>M</i>		2.36	2885	0.815
<i>L</i>		2.20	2890	0.791
<i>J</i>		2.16	2905	0.945
<i>S</i>		2.15	2925	0.752
<i>R</i>		2.06	2880	0.903
<i>N</i>		1.91	2885	0.852
<i>G</i>		1.59	3010	0.681
<i>H</i>		1.35	3040	0.770

* Keats and Herty: Elimination of Metalloids in the Basic Open-hearth Process.

These results have been obtained after due consideration of equilibrium conditions as specified earlier in the paper. The constant

$$K' = \frac{(\text{MnO})_{\text{slag}}}{(\text{Mn})(\text{FeO})_{\text{slag}}}, \text{ the concentrations expressed as already shown.}$$

The effect of temperature is very evident from these results. Furthermore, with the exception of heats *G* and *H*, the constant K_{Mn} decreases with increasing basicity. However, both factors vary simultaneously and it is difficult to show the exact relationship between them. These

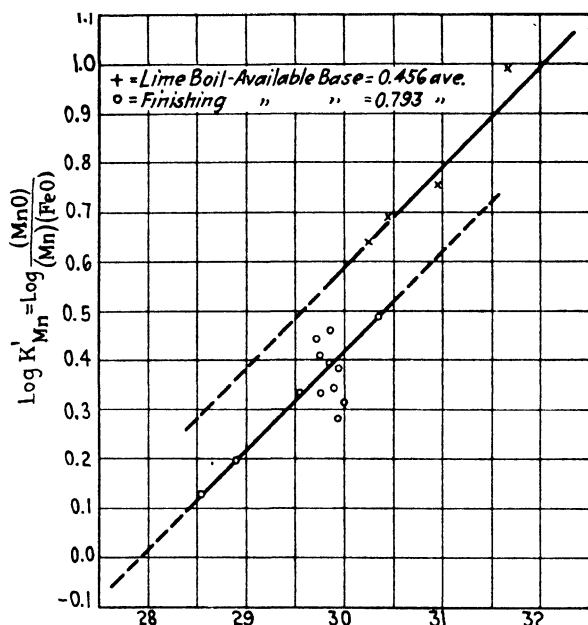


FIG. 1.—EFFECT OF TEMPERATURE ON MANGANESE EQUILIBRIUM.

data, combined with data from the "lime boil" period will show the effect of both basicity and temperature. Neglecting temporarily the effect of available base, K'_{Mn} may be plotted against $\frac{1}{T}$ to show the effect of temperature. This is shown in Fig. 1, the average available base being 0.783. The variation in the group of points at $\frac{1}{T}$ 29.70 to 30.00 is due to normal variation in temperature between slag and metal and to the variation in the basicity of the slags.

Equilibrium during the "Lime Boil"

In considering equilibrium during the early stages of the process two types of charges must be considered: (1) Those in which no ore is added with the scrap and which are not heavily oxidized during melting; (2) Those in which ore is added or in which the scrap is so heavily oxidized that a large percentage of iron oxide is found in the slag formed after the addition of the hot metal. The amount of iron oxide in the slag during this early period will be dependent upon:

1. Amount of ore charged.
2. Type of scrap charged.
3. Composition of iron charged.
4. Length of time taken for melting.
5. Temperature during melting period.

On account of these five factors, the iron oxide content of the first slags formed, and of the slags during the lime boil, will vary tremendously

During the lime boil the metal and slag are almost always in equilibrium, due to the intimate mixing resulting from the boil. The results shown in Table 6 have been obtained for this period.

TABLE 6.—*Results During the Lime Boil*

Heat No.	Sample No.	K'_{Mn}	Temperature of Slag Degrees F.	Available Base
<i>B</i>	8	9.75	2700	0.440
<i>E</i>	2	8.40	cold	0.382
<i>A</i>	8-16	5.70	2775	0.415
<i>F</i>	4	5.30		0.498
<i>C</i>	9	4.88	2830	0.430
<i>D</i>	10	4.35	2850	0.539

The effect of temperature is again very clearly shown in this table. If $\log K'_{Mn}$ plotted against $\frac{I}{T_{OF\text{ abs.}}}$ (Fig. 1) a straight line results. This is permissible since the basicity of the slags on these heats varies but little, averaging 0.456.

The numerical value of K'_{Mn} being much higher for this period than for finishing conditions means that for a given iron oxide content of the slag, manganese will have been much more completely eliminated at this time. This large elimination of manganese is always true when ore is charged with the scrap, the low temperature, low basicity and high iron oxide content of the slag all favoring the elimination of manganese.

Effect of Temperature

From the data on Fig. 1 the heat of the reaction may be calculated. The integrated form of the Van't Hoff isochore is:

$$\log_e \frac{K_1}{K} = \frac{Q}{R} \left(\frac{1}{T} - \frac{1}{T_1} \right) \quad (A)$$

Let us take the temperature range 2900° to 3000° F. to find the heat of the reaction $\text{Mn} + \text{FeO} = \text{MnO} + \text{Fe}$. The value found will be applicable over the entire temperature range studied.

For comparison with other data the heat of the reaction will be calculated in Centigrade units, *i. e.*, gram calories per gram mol. The temperatures therefore must be expressed as degrees Centigrade absolute.

$$\begin{aligned} \text{Data:} \quad R &= 1.99 \text{ calories} \\ T_1 &= 2900^\circ \text{ F.} = 1867^\circ \text{ C. absolute.} \\ T_2 &= 3000^\circ \text{ F.} = 1923^\circ \text{ C. absolute.} \\ K'_{Mn_1} &= 2.39 \\ K'_{Mn_2} &= 1.57 \end{aligned}$$

Substituting in equation A, $Q = 53,800$ gm. cal. per gm. mol, which means that the reaction evolves 53,800 gm. cal. per gm. mol over the temperature range 2600° to 3050° F. (1485° to 1675° C.), the range covered by the experimental work.

The heat of reaction, calculated from heats of formation at room temperature,¹³ is 25,200 gm. cal. per gm. mol. Since both MnO and FeO are dissolved in the metal in proportion to their respective concentrations in the slag, the discrepancy between the values 53,800 and 25,200 must be in the relative change in solubility of the two oxides with increasing temperature. If, as in the calculation above, 2900° F. be taken as a basis and the constant K'_{Mn_1} be calculated from the heat of reaction at room temperature, we obtain the value 1.97 against 1.57 observed. That is, if both oxides changed solubility at the same rate with increasing temperature we would expect K'_{Mn_1} to be 1.97, whereas we actually get 1.57, which means that FeO increases in solubility with rising temperature faster than MnO by the ratio $\frac{1.97}{1.57} = 1.25$.

Furthermore, since the manganese content of the metal depends on the concentration of MnO and FeO in the slag and in the metal it follows that the amount of iron oxide in the metal does not depend on the manganese in the bath, but is controlled by both manganese and MnO content, since the ratio $\frac{(\text{MnO})}{(\text{Mn})(\text{FeO})}$ must be constant for a given temperature. Since the concentration of MnO in the metal depends on the concentration of MnO in the slag, it is possible to have the same concentration of FeO in the metal with 0.10 per cent. Mn as with 0.40 per cent. Mn, pro-

¹³ Richards: "Metallurgical Calculations," 18.

vided only that the concentration of MnO in the slag is four times as high in the second case as in the first.

Residual manganese does not, therefore, serve as a "protector" against oxidation of the metal. High residual manganese may denote a bath low in iron oxide, but the low iron oxide in the bath is the agent for, and not the result of, high residual manganese.

The beneficial results of high manganese charges are:

1. Increased fluidity of the slag, enabling a more basic slag to be carried than with low manganese, and increasing the speed of working.
2. Increased ratio of MnS to FeS in the metal, giving the final addition of manganese a better chance to "clean up" more FeS than would be the case with low manganese.
3. Lower amounts of manganese necessary in the final additions than with low manganese.

Effect of Basicity of the Slag

The equilibrium constant for the third reaction by which manganese is eliminated is:

$$K = \frac{(\text{MnO} \cdot \text{SiO}_2)}{(\text{MnO})(\text{SiO}_2)}$$

This involves three unknown quantities and, therefore, cannot be evaluated. We may, however, determine the effect of free or dissociated SiO_2 in the slag by assuming it to be inversely proportional to the available base in the slag and determining the effect of available base on the constant,

$$K'_{Mn} = \frac{(\text{MnO})_{\text{slag}}}{(\text{Mn})(\text{FeO})_{\text{slag}}}$$

The lines drawn through the experimental points for finishing conditions and for the lime boil (Fig. 1) are practically parallel and from them the effect of basicity on the equilibrium may be shown. The expression $K''_{Mn} = K_{Mn}'(A. B.)^n$ will give the effect of available base if n is known. This equation may be written as $\log K''_{Mn} = \log K_{Mn}' + n \log (A. B.)$ and if $\log K'_{Mn}$ be plotted against $\log (A. B.)$, we may obtain n by finding the slope of the line. From such a plot we obtain $n = 0.65$ whence $K''_{Mn} = K'_{Mn} (A. B.)^{0.65}$ for any given temperature. If $\log K''_{Mn}$ be plotted against $\frac{1}{T^\circ F_{\text{abs.}}}$, we may obtain the effect of both temperature and basicity in one equation. This is shown in Fig. 2. The equation of this line is $\log K''_{Mn} = \left[\left(\frac{1}{T} \times 10^5 \right) - 28.25 \right] \frac{1}{5}$. This plot correlates all the variables with which we have dealt in the elimination of manganese in the basic open-hearth process, namely, manganese in the metal, FeO in the slag, MnO in the slag, basicity of the slag and temperature, and enables one to calculate very closely the amount of manganese that will

be present in the metal if the composition of the slag and the temperature be known.

Up to the time of tapping it is impossible to determine the metal temperature by pyrometric methods. The metal is almost always at a lower temperature than the upper layers of the slag, the exception being when the slag has been allowed to cool off by reducing the amount of fuel. By the use of the equation given above, the temperature of the slag-metal interface may be calculated if the slag composition and the manganese content of the metal are known. This calculated temperature will be

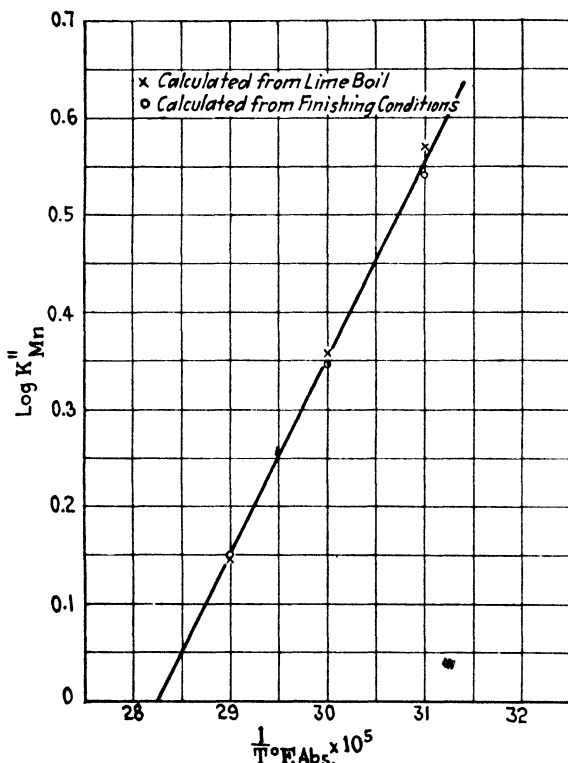


FIG. 2.—EFFECT OF TEMPERATURE AND BASICITY OF SLAG ON MANGANESE EQUILIBRIUM.

used in the sections on carbon and phosphorus, as it is much more accurate than a temperature at the top of the slag, obtained by an optical pyrometer.

Effect of Large Amounts of P_2O_5 in the Slag

In all of the heats studied the ratio of SiO_2 to P_2O_5 has been high. If we express this ratio as $\frac{\text{mols SiO}_2}{\text{mols SiO}_2 + \text{mols P}_2\text{O}_5} \times 100$, which is the silica expressed as per cent. of the total acids present, the average ratio for all

the heats studied is about 95 per cent. In these slags most of the combined MnO must exist as manganese silicate. Recalculations of data from European practice show that when this ratio is small, the equilibrium constant for manganese is much smaller than in the heats recorded in this paper. Typical examples are shown in Table 7.

TABLE 7.—*Recalculations of Data*
Tapping Temperatures

Source of Data	K'_{Mn}	SiO_2 as Per Cent. of Total Mols of Acid
This paper.....	2.20	95
Peterson ^a	1.60	86
Peterson ^a	1.24	75
Barberot ^b	1.23	68
Colcough ^c	1.47	68
Colcough ^c	1.67	64
Colcough ^c	1.48	64
Low Temperatures		
This paper.....	4.0 to 5.0	93
Colcough ^c	2.39	80
Colcough ^c	1.67	65
Colcough ^c	1.20	55
Very Low Temperatures		
Peterson ^a	1.55	54
Peterson ^a	2.12	50
Peterson ^a	2.29	46

^a *Rev. Metal Mem.* (1910) 198.

^b "Fabrication de l'Acier."

^c *Jnl Iron and Steel Inst.* (No. 1, 1924).

The absence of temperature data on these heats makes it impossible to determine quantitatively the effect of increasing amounts of P_2O_5 in the slag. That this effect is large as the P_2O_5 in the slag becomes high is very evident from the data given above. This leads to the conclusion that manganese phosphate is much more easily reducible by iron than manganese silicate and that, other conditions being equal, the higher the P_2O_5 in the slag the more residual manganese the metal will contain.

The constant K' $K'_{Mn} (A. B.)^{0.65}$ and its variation with temperature, as shown in Fig. 3, enables us to calculate very closely the amount of manganese that will be present in the metal under any conditions except where large amounts of P_2O_5 are contained in the slag. When the P_2O_5 content does not exceed about 5 per cent., the constant contained in this paper will hold for any basic slag and for any temperature up to 3100° F. The amount of manganese in the charge to give any desired residual manganese may also be calculated.

Example 1.—Calculation of Residual Manganese

Assumed data—Charge 250,000 lb. averaging 1.00 per cent. Mn

Products 25,000 lb. slag containing
 10 per cent. FeO
 3 per cent. Fe₂O₃ } = 0.196 mols FeO

A. B.
 0.800 mols 100-wt. unit of slag
 240,000 lb. steel.

Tapping temperature = 2900° F. $\left(\frac{1}{T^{\circ}F_{\text{abs.}}} \times 10^5 = 29.80 \right)$ K'_{Mn} at 2900° F. = 2.05 = $K'_{Mn} (A.B.)^{0.65}$

$$K'_{Mn} = \frac{2.05}{(0.800)^{0.65}} = \frac{2.05}{0.865} = 2.37 = \frac{(\text{mols MnO})}{(\text{per cent. Mn})(\text{mols FeO})}$$

expressing mols $\frac{\text{MnO}}{100\text{-wt. units}}$ as per cent. Mn

$$\text{mols MnO} = \frac{\text{per cent. Mn}}{54.9}$$

we have $\frac{\text{per cent. Mn}_{\text{slag}}}{\text{per cent. Mn}_{\text{metal}}} = 2.37 \times 54.9 \times 0.196 = 25.5$ The total pounds of manganese are 250,000 \times 0.01 = 2500Let x = pounds manganese in the metal2500 - x = pounds manganese in the slag

$$\frac{100(2500 - x)}{25,000} = \frac{100x}{240,000} = 25.5$$

whence x = 682 lb. Mn in the metal = 0.28 per cent. Mn.2500 - x = 1818 lb. Mn in the slag = 7.25 per cent. Mn

NOTE: This calculation does not take into account volatilization of manganese, which will amount to approximately 5 per cent. of the manganese charged.

CARBON

Reactions (4) $C + \text{FeO} = \text{CO} + \text{Fe} - \text{cal. (FeO in metal)}$ (5) $C + \text{FeO} = \text{CO} + \text{Fe} - \text{cal. (FeO in slag)}$

Since these reactions are endothermic, increasing temperature will drive them to the right, more carbon being removed for a given FeO content of the slag at a high temperature than at a low one. If the solubility of CO changes with temperature, this will throw the reaction either to the right or the left, depending on the change in solubility.

The true equilibrium constant for the reaction is:

$$K_c =$$

For any given temperature, (CO) being constant, $K'_c = \frac{1}{(C)(FeO)}$, (E)
 where $K'_c = \frac{K_c}{(CO)}$.

Since the quantitative relationship between solubility of CO and temperature is not known, it will be necessary to incorporate the term (CO) in the constant K'_c . The Van't Hoff isochore does not apply to this constant, since we are calculating an empirical, rather than true, equilibrium constant.

Laboratory Experiments

Experiments on the reaction in the metal phase have given the following results:

1. Solubility of CO at 2700°–2800° F. = 0.018 per cent. by weight¹⁴
2. The constant $K_c = 0.36$ at 2700° to 2800° F.

when all concentrations are expressed as weight per cent.

Combining the two results, we obtain:

$$K'_c = \frac{1}{(C)(FeO)} = 20 \text{ at } 2700^\circ \text{ to } 2800^\circ \text{ F.}$$

From this constant the amount of dissolved FeO corresponding to any carbon content may be calculated for the temperature range given above.

Determinations of the solubility of FeO in pure iron have given averages of 1.22 per cent. and 0.97 per cent. at 2700° to 2750° F. on two separate investigations. In the experimental work it was certain that the first determinations were made at a slightly higher temperature than the second, the crucibles in the second series being very often heavily skulled, whereas this took place only rarely in the first series. It is therefore due to the higher temperature that the solubility in the first series is higher than that obtained in the second.

Using the value 0.97 per cent., iron at 2700° to 2800° F. may contain 0.052 per cent. carbon when saturated with FeO. As the temperature rises, the numerical value of the constant K'_c will increase due to the endothermicity of the reaction, and the amount of carbon in equilibrium with iron saturated with iron oxide will decrease.

Plant Data

In the experimental work on large furnaces, determinations of the oxygen content of the metal have not been made. However, this content must be proportional to the iron oxide content of the slag if equilibrium between slag and metal is reached. The proportionality constant, or distribution ratio, of iron oxide between slag and metal must be equal, for the same temperature, to the ratio found in the laboratory furnace

¹⁴ H. B. Cobb: Master's Thesis, Mass. Inst. Tech., 1923.

where the slag was composed entirely of iron oxide. The results given in Table 8 have been obtained where equilibrium has been established between slag and metal.

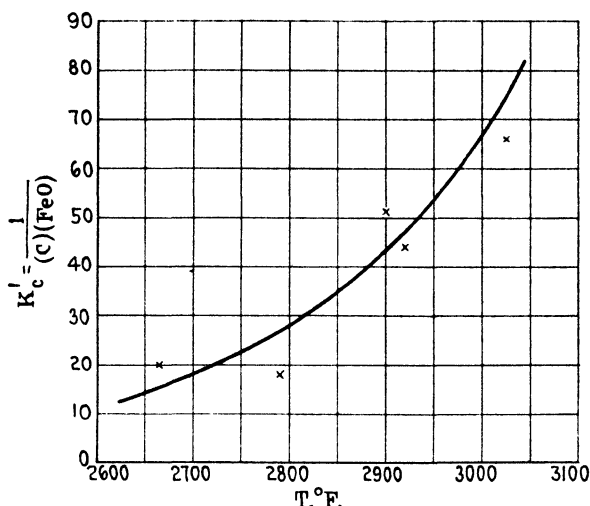


FIG. 3.—EFFECT OF TEMPERATURE ON CARBON EQUILIBRIUM.

These results are shown graphically in Fig. 3, K'_c being plotted against temperature. More data are needed before the exact curvature of this line can be established. Unfortunately we have no means of cor-

TABLE 8.—Results When Slag and Metal are in Equilibrium

Heat	Sample	Condition of Heat	K'_c	Temp.,* Degrees F.
A	8-16	Lime Boil	16.7	2790
B	8	Lime Boil	20.2	2665
B	17	Working. Before small hot metal addition	44.0	2920
M		Finishing	50.3	2900
G		Finishing	65.6	3025

* Temperature calculated from manganese constant, K''_{Mn} .

recting for the solubility of CO, as we have in the case of manganese, where the concentration of MnO in the metal is proportional to the concentration of MnO in the slag.

The temperatures during the lime boil are very close to those in the laboratory experiments and the concentration of CO should be the same in both cases. Using the data of Table 8, we may calculate the amount of FeO in the metal from the distribution ratio, and from equation (E).

The two methods of calculation give fairly close agreement at these temperatures.

Heat	Sample	Per Cent. FeO in Metal	
		Calculated from Distribution Ratio	Calculated from Equation (E)
A	8-16	0.030	0.036
B	8	0.034	0.047

From Fig. 3 we may semi-quantitatively determine any one of three variables, carbon, FeO in the slag, or temperature, if the other two are given and if the metal and slag are in equilibrium.

Example 1.—Calculation of the amount of FeO necessary to eliminate carbon to a given point at a given temperature.

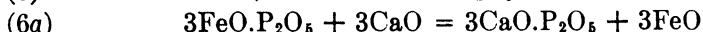
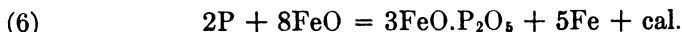
For this we will take a low carbon content, 0.03 per cent., at 3000° F. K'_c at 3000° = 68, whence the mols of FeO in the slag = $\frac{1}{7}$ 0.490. This equals 35.2 per cent. total FeO in the slag, (0.490) (71.8) = 35.2.

Example 2.—Calculation of the amount of carbon that will be in the metal at 2900° F. when the slag contains 15 per cent. total FeO = 0.209 mols FeO. At 2900°, K'_c = 43.5, whence

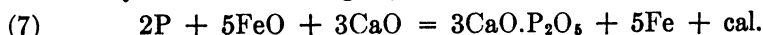
$$\text{per cent. carbon} = \frac{1}{(43.5)(0.209)} = 0.110 \text{ per cent.}$$

PHOSPHORUS

The reactions by which phosphorus is eliminated are:



which may be combined to give,



This reaction is strongly exothermic; therefore, phosphorus is much easier to eliminate at low temperatures than at high temperatures. The equilibrium constants for these reactions are:

$$(6) \quad K_{1P} = \frac{(3FeO.P_2O_5)}{(P)^2 (FeO)^3} \quad (F)$$

$$(6a) \quad K_{2P} = \frac{(3CaO.P_2O_5) (FeO)^3}{(3FeO.P_2O_5) (CaO)^3} \quad (G)$$

$$(7) \quad K_{3P} = \frac{(3CaO.P_2O_5)}{(P)^2 (FeO)^5 (CaO)^3} \quad (H)$$

For a given amount of phosphorus in the charge and a given slag and metal weight, the extent of elimination will depend on the concentration

of iron oxide and available base in the slag and on the temperature.

In determining the equilibrium constants for the reactions given above the utmost care must be taken in determining the concentrations of the reacting substances. The three factors in the denominator of the constant for reaction 7 are raised to the second, fifth and third powers, and this magnifies any experimental error tremendously. At very low phosphorus concentrations this is particularly true.

Laboratory Experiments

These were carried out to determine the extent of elimination of phosphorus with slags containing only iron oxide and ferrous phosphate (reaction 6). Electrolytic iron, to which had been added 0.0 to 8.0 per cent. phosphorus, was melted in the resistance furnace, and slags containing iron oxide only and mixtures of iron oxide and ferrous phosphate were added when the metal was molten. The reaction was allowed to proceed for about an hour and the metal was then cast. The experimental work showed clearly that the runs made with very low phosphorus in the charge had not been left in the furnace long enough for equilibrium to be established, the same being true of the runs with very high phosphorus in the charge. The metal and slag analyses and the composition of the charge on the four runs which reached equilibrium are given in Table 9.

TABLE 9.—*Metal and Slag Analyses and Composition of Charge*

Run No.	Metal Per Cent. P	Charge Per Cent. FeO	Slag Per Cent. P_2O_5	Analysis at Equilibrium		
				Metal Per Cent. P	Slag	
					Per Cent. FeO	Per Cent. P_2O_5
7	7.00	100	0.0	4.99	75.5	24.5
33	3.80	83.5	16.5	3.42	80.6	19.4
34	5.50	84.5	15.5	3.64	78.3	21.7
35	7.70	86.5	13.5	3.87	77.5	22.5

The equilibrium constant, K_{1P} $\frac{(3FeO.P_2O_5)}{(P)^2 (FeO)^3}$, is

RUN No.	K_{1P}
7	0.095
33	0.089
34	0.074
35	0.097

Average

0.089 at 2750° F. (F)

when (P) = per cent. by weight.

$(3FeO.P_2O_5)$ = mol fraction

(FeO) = mol fraction free FeO.

Since the slags contained only FeO and ferrous phosphate, the free FeO could be easily calculated. To convert this constant to terms that may be used in comparison with open-hearth slag composition, we transfer mol per cent. to mols per 100-wt. units, the result being $K_{1P} = 0.56$ for these concentration terms.

We have assumed that all of the FeO in open-hearth slags is "free" as far as reaction with the metalloids is concerned, and in calculating the amount of ferrous phosphate to be found in these slags we may use the "total FeO" as in the sections on carbon and manganese. Let us take an open-hearth slag analyzing 10 per cent. FeO, 2 per cent. Fe_2O_3 and 2 per cent. P_2O_5 , with 0.020 per cent. P in the metal. The total mols of FeO are $(0.139 + 0.038) = 0.177$.

$(3\text{FeO} \cdot \text{P}_2\text{O}_5) = (0.56) (0.02)^2 (0.177)^3 = 0.21 \times 10^{-9}$ mols per 100-wt. units of slag $= 0.30 \times 10^{-7}$ per cent. P_2O_5 . This is negligible compared to the total P_2O_5 in the slag, which is practically all present as calcium phosphate.

Plant Study

The results for reaction 7 given in Table 10 have been obtained for finishing conditions in the open hearth.

TABLE 10.—*Finishing Conditions*

Heat	Sample	$\times 10^{-4}$	Temp., Degrees F*
Q	33	18.70	2890
L		15.40	2920
K		13.70	2865
A		13.50	2895
J		12.60	2900
P		8.15	2865
S	17	5.05	2930
B		3.82	2920
G		2.24	3025
H		0.78	3045

* Calculated from the manganese constant K''_{Mn} .

The results for this reaction during the lime boil are:

Heat	Sample	$K_{1P} \times 10^{-4}$	Temp., Degrees F*
B	8	309	2665
E	2	114	2715
A	8-16	94	2790
F	4	40	2780

* Calculated from the manganese constant K''_{Mn} .

From this table, the effect of temperature can be very plainly seen.

Fig. 4 shows $\log (K_{3P} \times 10^{-5})$ plotted against $\frac{1}{T^{\circ}F. - 459.67}$. The heat of reaction, calculated as shown previously, is +209,000 calories per mol.

This brings out clearly why phosphorus is so very readily eliminated at low temperatures. When high temperatures are carried in the furnace, either the basicity of the slag or its iron oxide content must be very high in order to carry out the desired elimination, whereas at low temperatures a large amount of phosphorus may be eliminated though the slag is very

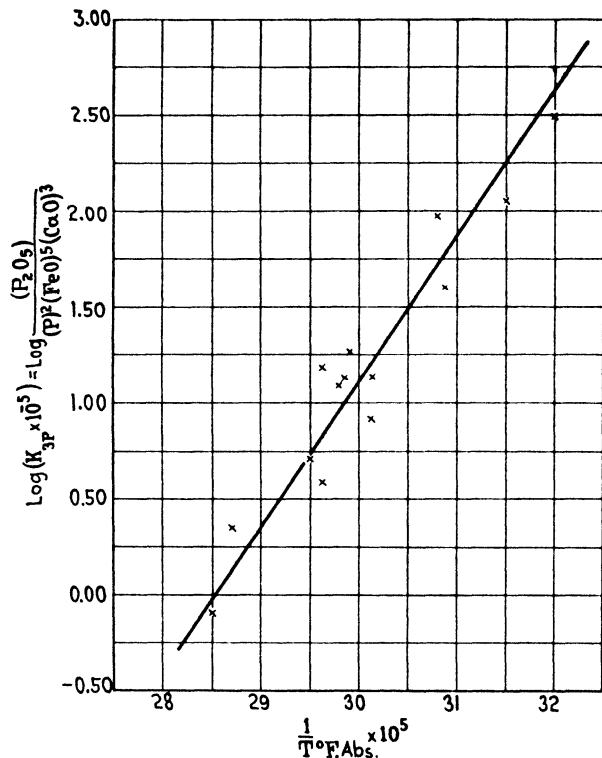


FIG. 4.—EFFECT OF TEMPERATURE ON PHOSPHORUS EQUILIBRIUM.

weakly basic. The equation connecting the equilibrium constant with temperature is

$$\log (K_{3P} \times 10^{-5}) = \left(\left(\frac{1}{T} \times 10^5 \right) - 28.52 \right) \left(\frac{1}{1.322} \right). \quad (H_1)$$

From these results the amount of phosphorus that can be eliminated under any slag conditions and at any temperature may be readily calculated. If it is desired to determine the amount of phosphorus that may be eliminated for a given phosphorus content of the charge, or, conversely, the allowable amount of phosphorus in the charge for a given phosphorus content at the end of the heat, the metal and slag weight, slag composition and temperature must be predetermined, or approximated. The utility

of this equation is being tested on a 200-ton furnace and the results to date are shown in Table 11.

TABLE 11.—*Phosphorus in Charge*

Heat No.	Per Cent. Metal in Charge	Per Cent. Si in Metal	Per Cent. P Predicted	Per Cent. P Obtained
1	22.4	0.84	0.011	0.012
2	31.0	1.54	0.012	0.012
3	25.0	1.25	0.010	0.010
4	20.0	1.12	0.013	0.012
5	19.0	0.84	0.014	0.013
6	19.7	1.35	0.009	0.015
7	22.0	1.00	0.010	0.010

The method of testing is to calculate the amount of lime necessary, estimating the silicon content of the iron that is to be charged, to bring the phosphorus to about 0.012 per cent., and then correct for the actual silicon content of the metal when the charging has been completed, and compare the calculated phosphorus content of the bath with that obtained in the preliminary tests taken from the furnace.

The iron oxide content of the slag is calculated from Fig. 3 by the per cent. carbon at which the heat is to be tapped and the tapping temperature. The test is being carried out under normal operating conditions, and the results given above are on consecutive heats. An example of the general method of using the equation is given below.

Example.—To determine the amount of phosphorus at the end of the heat for a given phosphorus content in the charge:

Assumptions:

Weight of charge = 250,000 lb., with 0.10 per cent. P

Weight of steel = 240,000 lb.

Weight of slag = 25,000 lb.

Available base = 0.800 mol per 100-wt. units

Per cent. FeO in slag = 10.0

Per cent. Fe₂O₃ in slag = 3.0

$$\text{Temperature} = 2900^{\circ} \text{ F.}, \left(T^{\circ} \frac{1}{F_{\text{abs}}} \times 10^5 = 29.8 \right)$$

From these assumptions, the mols FeO per 100-wt. units of slag = 0.196, and K_{3P} , from Fig. 4 or equation $(H_1) = 8.93$, whence $\frac{(P_2O_5)}{(P)^{\frac{5}{2}}} = (8.9)$ $(0.800)^3(1.96)^5 = 131$. Expressing P₂O₅ as per cent. P instead of mols P₂O₅, $\frac{(P)^{\frac{5}{2}}}{(P)^2_{\text{metal}}} = 8,130$. The total pounds of phosphorus in the charge = 250.

Let x = pounds of phosphorus in the metal.

Then $(250 - x)$ = pounds of phosphorus in the slag, whence

$$\frac{(250 - x)(100)}{25,000} = \frac{\left(\frac{100x}{240,000}\right)^2}{8,130}$$

Solving this equation, $x = 25.2$ lb. phosphorus in the metal

$250 - x = 224.8$ lb. phosphorus in the slag,

whence per cent. P in metal = 0.0105

per cent. P_2O_5 in slag = 2.06

This method is applicable to the range of slag compositions and temperatures given in this work.

CONCLUSIONS

1. The amount of residual manganese, excepting when the slag contains over 5.0 per cent. P_2O_5 , is controlled by the total manganese charged, the amount of manganese volatilized, the iron oxide content of the slag, the basicity of the slag, the slag volume, and temperature.

2. The quantitative relationship between these variables, excepting volatilization, is:

where $K_{Mn}'' = \frac{(MnO)}{(Mn)(FeO)} (Available\ Base)^{0.65}$, the slag concentrations being expressed as mols per 100-wt. units and the metal concentrations as weight per cent. $T = ^\circ F$ abs.

3. From a consideration of the heat of the reaction



as calculated from plant data and as calculated from heats of formation at room temperature, the solubility of FeO increases 1.25 times as fast as the solubility of MnO for a given increase in temperature.

4. The amount of iron oxide in the metal is not controlled by the residual manganese present.

5. The amount of carbon in the metal depends on the concentration of iron oxide in the slag and on the temperature.

6. At $2700^\circ - 2800^\circ F.$ the equilibrium constant for the reaction $C + FeO = CO + Fe$ in the metal phase is:

$$\frac{(CO)}{\sqrt{(FeO)}} = 0.36,$$

when all concentrations are expressed as weight per cent.

7. The solubility of CO in pure iron at 2700° to $2800^\circ F.$ equals 0.018 per cent. by weight.

8. The amount of phosphorus in the metal depends on the total phosphorus in the charge, the iron oxide content of the slag, the basicity of the slag, the slag volume and the temperature.

9. The quantitative relationship between these variables is:

$$\log (K_P \times 10^{-5}) = \frac{1}{7.0 \times 10^4} \left(\frac{1}{T} \times 10^5 - 28.52 \right) \left(\frac{1}{1.322} \right)$$

when slag concentrations are expressed as mols per 100-wt. units, metal concentration expressed as weight per cent. and temperature T as degrees Fahrenheit absolute.

10. The heat of the reaction $2P + 5FeO + 3CaO = 3CaO.P_2O_5 + 5Fe$ equals + 209,000 calories per mol.

11. The utility of the equation for the phosphorus equilibrium is being tested and the first results have given remarkable agreement between the predicted phosphorus content of the bath and that obtained on the heats tested.

ACKNOWLEDGMENT

The author wishes to express his appreciation of the assistance rendered by students of the Massachusetts Institute of Technology School of Chemical Engineering Practice, and to acknowledge the cooperation of the open-hearth department of the Lackawanna Plant of the Bethlehem Steel Co.

DATA

Heat	Sample	Metal						Slag				
		C	Mn	P	S	P ₂ O ₅	SiO ₂	FeO	Fe ₂ O ₃	MnO	CaO	MgO
A	8-16	0.829*	0.206	0.0357*	0.0317	4.41	Average of	samples 8	to 16, on	this heat		
A	25	0.649*	0.287	0.0164*	0.0287	4.27	18.55	13.94	2.78	14.54	38.66	5.87
A	28	0.222*	0.242	0.0096	0.0228	3.71	18.20	9.22	2.47	11.11	45.14	6.07
A	33	1.07	0.379	0.0717	0.0423	3.71	15.86	11.12	3.12	9.13	47.83	6.00
B	8	0.323*	0.159	0.0074*	0.036	3.35	33.05	3.17	0.12	12.04	38.50	9.40
B	13	0.320*	0.194	0.0088*	0.027	2.85	16.54	11.69	5.81	9.13	44.25	5.78
B	15	0.084	0.183	0.0078	0.022	2.56	15.62	10.18	5.63	7.93	46.90	6.46
B	17				0.066	3.64	28.38	11.94	5.48	7.45	47.70	6.06
C	5		0.110		0.054	3.02	28.18	9.50	1.14	11.20	33.70	5.88
C	9		0.158		0.057	3.44	24.11	6.79	1.80	9.64	39.55	6.18
C	11		0.114		0.043	2.66	19.14	15.54	3.62	8.18	40.10	6.62
C	19		0.050		0.052	2.51	28.28	15.67	2.49	6.58	42.90	6.10
D	4		0.142		0.061	2.54	26.76	7.78	1.95	8.13	29.50	6.52
D	10					3.95	28.34	5.91	2.46	6.70	41.95	8.18
E	2	1.55*	0.240	0.0790		4.60	24.65	9.85	0.63	13.30	36.55	7.08
E	2	1.15*	0.125	0.0440*		4.60	24.65	9.85	1.72	11.92	37.35	7.58
F	3	1.47*	0.200	0.033		4.90	24.00	8.02	1.70	11.08	39.30	7.64
G		0.056	0.231	0.0126	0.056	2.38	19.86	8.79	7.93	7.25	45.60	5.78
H			0.182	0.0079	0.037	2.09	16.96	10.91	11.33	6.73	47.20	5.48
J			0.265	0.0059	0.030	1.94	13.76	7.77	5.27	8.38	54.55	5.48
K			0.119	0.0075	0.041	1.96	20.38	10.05	3.44	5.24	44.97	10.86
L			0.231	0.0148	0.040	2.14	21.08	6.55	1.95	4.60	51.40	8.24
M			0.100	0.0166*	0.038	2.06	17.59	12.56	4.73	4.33	47.95	7.50
N			0.258	0.0077*	0.028	1.95	13.57	12.34	7.13	10.72	47.55	5.44
P			0.203	0.0158	0.044	1.86	20.74	8.40	3.05	7.76	45.66	8.44
Q			0.140	0.0081	0.045	1.86	20.22	8.49	3.94	4.95	48.20	8.64
R			0.103	0.0033*	0.028	1.77	11.51	18.05	9.45	6.41	44.90	6.98
S		0.07*	0.178	0.0194	0.039	2.76	19.42	7.08	4.80	5.11	50.83	6.18

* This metalloid is not at equilibrium.
Analyses for sulfur are included merely for the sake of reference as no mention has been made of the sulfur equilibrium in this paper. It is not to be understood that all these analyses represent equilibrium values.

DISCUSSION

H. STYRI, New York, N. Y.—Herty states that calculation of equilibrium in a steel melt by thermochemical methods is open to serious errors, because heats of reactions are largely unknown at the high temperatures. It should be remembered, however, that fair extrapolations of known physical data can be made, so that when proper assumptions and correct methods of calculation are used, the results should at least give an approximation of sufficient accuracy for practical purposes. The writer calculated,¹⁵ for instance, that under CO gas of 1 atmosphere pressure and 1600° C., the amount of carbon dissolved should be .009 per cent., which is equivalent to .021 per cent. CO in solution. (In a discussion for the Faraday Society, 1925, Herty has misquoted this value.) By experiment Herty found .018 per cent. With this agreement apparently both the writer's thermodynamical theory and the experimental work have been properly developed.

If wrong assumptions are made, no amount of correct physical constants can give reasonable results, except by accident, as for instance, when some kind of a formula is used for a reaction and calculation of a certain constant, and thereafter this constant is used for entirely similar reactions in the same formula. It is therefore plausible that Herty can get comparative results in some of his calculations.

On the other hand, when he presumes that the concentrations of MnO and FeO in metal are directly proportional to all MnO and FeO in the slag and that all FeO in the slag is available for reaction with the metalloids, although evidently the available active FeO or MnO must depend on SiO₂ or P₂O₅ present; when he further considers the lime boil period as equilibrium condition although both part of the lime and part of the metal are still unmelted and are furnishing a constant new supply of base to the slag and carbon to the melt, we can see cause why he found the heat of reaction of MnO twice as high as determined directly by experiment.

From his Table 7 can be deducted that the dissociation of manganese phosphate and manganese silicate must influence the equilibrium constant. If we consider this dissociation and use the "active" MnO and FeO in the formula for determination of *K*, this correction should allow finding *K* constant for one temperature even with such variable slag composition as Herty gives.

His calculations seem to lead to another apparently contradictory conclusion, when he on page 1123 finds that a steel saturated with FeO (.97 per cent. at 2700 to 2800° F.) can hold .052 per cent. carbon in solution, while he earlier in the same section, reports the solubility of CO to be .018 per cent., as found by experiments. If this latter determination

¹⁵ *Jnl. Iron and Steel Inst.* (1923) 218.

was made under atmospheric pressure, it agrees fairly with the writer's theoretical calculation, as referred to above, while the other composition given by Herty seems to be in error.

C. H. HERTY, JR., Pittsburgh, Pa. (written reply to discussion).—Reference to page 215, paragraphs 2 and 3 of Dr. Styri's paper,¹⁶ will explain the statement made by the writer as to the errors involved in a purely theoretical treatise on open-hearth reactions.

In these paragraphs Dr. Styri calculates that the amount of manganese found in the metal on a given steel heat should be .70 per cent. when LeChatelier's value for the heat of combustion is used, and .40 per cent. when Vologdin's value is used. In the five heats given in the appendix of his paper the residual manganese is .06, .05, .04, .06 and .10. Furthermore, there was very little change in the manganese content of the bath for the last hour of working, showing that the manganese must have been very close to equilibrium.

The value quoted by the writer in discussion for the Faraday Society is calculated from Dr. Styri's paper, page 209, third equation on this page.

The assumption that the concentration of FeO and MnO in the metal are directly proportional to all the MnO and FeO in the slag has been corrected by the basicity term in the equation for manganese equilibrium and is automatically corrected for in the phosphorus equation. The results showing $\log K$ plotted against $1/T$ justify this assumption.

In regard to the last paragraph of Dr. Styri's discussion, there is no reason why both CO and carbon should not be in solution simultaneously, in fact there is every reason why they should. As soon as CO is dissolved in pure iron the reaction $\text{CO} + \text{Fe} \rightarrow \text{FeO} + \text{C}$ takes place and at equilibrium, FeO, C and CO will be present in the iron.

¹⁶ *Jnl. Iron and Steel Inst.* (1923) 218.

Twenty-five Years of Metallography

BY WILLIAM CAMPBELL, SC. D., PH. D.,* NEW YORK, N. Y.

FIRST I must express my deep appreciation for the honor of being privileged to give the Howe Memorial Lecture this year and at the same time my feeling of inadequacy to do justice to the subject.

The first Howe lecturer was most fittingly, Professor Sauveur, his contemporary and friend, and the subject was beta iron. Last year the second Howe lecture was delivered by Dr. Mathews, one of his most distinguished pupils, who spoke on austenite. This year, the Howe Professor of Metallurgy was chosen to deliver the third annual lecture, and the subject ought to be martensite.

No one but Professor Sauveur could have brought to life what was considered by many to have been dead and buried, and he so persuasively and convincingly proved to us by his experiments the existence of something that the followers of that new cult "X-Ray and Crystal Structure" would have us believe is simply alpha iron. And Dr. Mathews from his wide practical experience was so easily able to convince us that austenite was not only the most wonderful of the iron-carbon series, but that it was the wonder alloy of the future.

If I were to follow in the footsteps of my distinguished predecessors, I would talk to you about martensite. But when I had planned this lecture, I found that I was writing about Professor Howe and his work and his influence on the science of metals of today, and that martensite had become the secondary theme. And when finally I was obliged to choose a title, I remembered that it was in 1901 I came from Roberts-Austen with a letter of introduction to his very dear friend, Henry Marion Howe, at the Columbia School of Mines, to continue my work at the next bench to Dr. Mathews. Since then a quarter of a century has gone by, and during that time all branches of science seem to have been remade, so great has been our advancement in knowledge and discovery. And now that Metallography has finally established its place as an important branch of science, with its own textbooks and literature, I would like to review what seem to me to be the most important advances we have made in the last 25 years. To do this, I would start with Howe's "Iron, Steel and Other Alloys," and end with Jeffries and Archer's "Science of Metals."

In the preface of the former, Professor Howe wrote:

My warmest thanks are due to the friends who have aided me with their counsel and knowledge. In particular, let me thank most sincerely Prof. Margaret E. Maltby

* Howe Professor Metallurgy, Columbia University; Advisory Metallurgist, U. S. Navy Yard, New York.

for examining the first seven chapters and the tenth, those relating to the genesis of alloys in general, and to the phase rule—and Dr. William Campbell, non-resident lecturer on Metallurgy, for much valuable information, for many of the micrographs and indeed for the original suggestion to write the book; though as to the last, my gratitude is somewhat mingled with reproach.

While the book was mainly devoted to iron and steel, it was the first to attempt to set forth our knowledge of alloys from the newer viewpoint of physical chemistry, and to stimulate an interest in this branch of metallurgy.

Another book I would like to mention, and quote from the preface is: "The Metallography of Steel and Cast Iron" by Henry Marion Howe, 1916; "an introduction to the new science of microscopic metallography as applied to steel and cast iron and an extended study of the very new branch of that science, the mechanism of plastic deformation."

Though I try to explain and illustrate clearly the visible phenomena, my chief aim is to stimulate others to think profoundly, in order that some among them may in due time push discovery farther and farther beyond its present very early state.

The true task of the teacher is to excite thought. Hence I do not hesitate to offer such hypotheses as I can devise, not in the belief—hope should not enter into consideration—that they will endure, but with the aim of stirring others to seek the truth by destroying them. This, I take it, is the true function of most hypotheses, and this purpose should be in the heart of every philosophic student.

Coming next to Jeffries and Archer's "Science of Metals," we had a great store of facts about the structure and properties of metals, and alloys, and a few theories scattered throughout the literature. A great amount of work had been done on the effect of cold work and of annealing on the structure and properties of metals, but the hardening due to cold work and the hardening of steel by quenching, were two very different things, while duraluminum was considered by many to be a freak alloy. Jeffries and Archer set out to give the "Reasons Why" underlying the science of metals. They set forth in a most logical manner the laws of grain growth and showed that ductility is due to ease of slip along certain crystallographic planes of weakness whereas hardening in all metals is caused by slip interference. Instead of there being anything mysterious about metals, once we accept the theories derived from X-ray analysis and atomic structure, the mechanism of deformation and of hardening is most simple. Professor Howe's influence on this work is given in a recent letter from Dr. Jeffries, from which I will quote later.

To cover the last 25 years of the science of metals would require ten times the amount of time allowed for this lecture, and I must be content with the mere mention of some of the outstanding points. This I will do under the following headings:

- (a) The structure of metals, the effect of strain and of annealing
- (b) The development of the iron-carbon diagram

(c) Martensite and the hardening of steel

(d) Progress in our knowledge of the constitution of alloys, as exemplified by the bronzes and brasses.

To realize the state of Metallography at the beginning of the century, we have only to turn to the first four volumes of the *Metallographist* edited by Professor Sauveur. I will mention a few of the outstanding papers therein:

Ewing and Rosenhain: The Crystalline Structure of Metals.⁽¹⁾

Osmond: On the Crystallography of Iron.⁽²⁾

Bakhuis-Roozeboom: Iron and Steel from the Point of View of the "Phase Doctrine."⁽³⁾

Stansfeld: The Present Position of the Solution Theory of Carbonized Iron.⁽⁴⁾

Stead: Iron and Phosphorous.⁽⁵⁾

Charpy: Study of White Alloys Called Antifricition.⁽⁶⁾

THE STRUCTURE OF METALS

Just as Ewing and Rosenhain's work marks the beginning of our modern knowledge of the structure of the non-ferrous metals, so does Sauveur's work on iron⁽⁷⁾ begin our study of abnormal grain growth.

From 1899 to 1901 I had been studying the dendritic structure of metals and the effect of cold work on structure, at the Royal School of Mines. Unfortunately, it was not until the work was practically completed that I became acquainted with Ewing and Rosenhain's results.

At the joint meeting of the Institution of Mechanical Engineers with the American Society of Mechanical Engineers at Chicago in June, 1904, the author read a paper entitled "The Effects of Strain and of Annealing in Aluminum, Antimony, Bismuth, Cadmium, Copper, Lead, Silver, Tin and Zinc." This was a summary of various papers handed in by Sir William Roberts Austin in October, 1901, covering work done under his direction at the Royal School of Mines between September, 1899 and June, 1901, and forming Appendix IV to the Sixth Report to the Alloys Research Committee.

The structures found on the surfaces of small ingots were studied and the effect of slight strain was observed by examining the surface of a small bar or ingot after bending to a slight angle and straightening again. The effects of great strain were found on examining the structure of ingots after hammering or rolling. The samples were then annealed, repolished and etched and the effects of annealing observed.

In rolled copper the grains were drawn out and elongated but in the case of the softer metals such as lead, tin, zinc and cadmium, rolling or hammering was found to break down the original crystals and produce a finer crystallization. We now know that this is due to the fact that the equiaxing temperature of these soft metals is so low that rolling or ham-

¹ Numbers in parenthesis refer to list of books and publications on page 1175.

mering at room temperature is really hot working, hence the fine-grained structure.

The amorphous metal hypothesis was set forth by Beilby⁽⁸⁾ in 1911 to explain the hardening due to cold work, and this was extended by Rosenhain and Ewen⁽⁹⁾ in 1912.

The effect of cold work and annealing in the physical properties of copper and brass was given in Grard's admirable paper⁽¹⁰⁾ in 1909, and this gave us the type curves with which we are all so familiar.

Howe's "Metallography of Steel and Cast Iron," already referred to, was written in 1915.

In 1915 Mathewson and Phillips' paper⁽¹¹⁾ before this Institute on the "Recrystallization of Cold Worked Alpha Brass on Annealing" caused a very general interest in the structure of metals. This was discussed by Jeffries and followed in 1917 by two other noteworthy papers, namely that by Jeffries⁽¹²⁾ on "Grain Growth Phenomenon in Metals" and by Howe⁽¹³⁾ "On Grain Growth." Lastly, we had Jeffries and Archer's "Slip Interference Theory of Hardening" in 1921, and the whole subject was admirably set forth by them in their book "The Science of Metals," in 1924. The following summarizes what they say:

Summary of the Slip Interference Theory of Hardening

The metal at the grain boundaries is substantially amorphous, possessing the essential deformational and strength characteristics of typical vitreous amorphous material.

Plastic deformation below the temperature of recrystallization generates additional amorphous metal at the boundaries of the original grains.

Even the most severely cold worked metals are predominantly crystalline.

The formation of vitreous amorphous metal on all slip planes, as postulated by Beilby, is not tenable. Further slip on "used" planes must occur in the course of maximum deformation.

The importance attached to the specific hardness of amorphous metal as a cause of hardening has been greatly exaggerated.

Strain hardness is caused by slip interference created by grain fragmentation of the original grains.

Summary of Law of Grain Growth

The laws of grain growth they have set forth as follows:

The grain size of cast metals is usually smaller, the more rapid the rate of solidification.

The grain size in cast metals which undergo no phase change in the solid state cannot be changed appreciably by heating below melting point.

Grain growth in the solid state may occur in (a) worked metals; (b) compressed powders; (c) electrodeposited metals; (d) in iron when it changes allotropic form; and (e) in alloys in which a new phase is formed in the solid state.

The recrystallization temperature is lower (a) the greater the amount of deformation, (b) the smaller the grains prior to deformation, (c) the purer the metal, (d)

the lower the temperature at which the deformation is effected, and (e) the longer the time of heating.

In any given metal the grain size, after complete recrystallization, is normally smaller the lower the recrystallization temperature.

Above the recrystallization temperature, the grain size is normally greater the higher the temperature and the longer the exposure.

The higher the temperature the more rapid the grain growth.

Certain conditions of non-uniformity sometimes give rise to the formation of abnormally large grains. This is "germination." These are (a), grain-size contrast; (b), strain gradients; (c), temperature gradients; (d), concentration gradients; and (e), obstruction gradients.

The presence of foreign matter, or a second phase, introduces mechanical obstruction to grain growth. Resistance increases as the quantity of foreign matter or other phase increases and as the particle size decreases.

The presence of a certain amount of obstruction matter increases germination.

The higher the germinative temperature, the larger will be the grains and the quicker will they form.

The more rapid the heating through the germinative temperature range, at least within limits, the finer will be the grain size.

Although Jeffries' views on the manner in which germination occurs are generally accepted in this country, namely that it is a true recrystallization followed by abnormal grain growth of certain favored grains, another view has been put forward by Carpenter and Elam⁽¹⁴⁾ from their study of tin and aluminum. Within a certain narrow range of cold work, grain growth occurs in certain grains by invasion of their neighbors, and this without previous recrystallization. When the cold work reaches a definite amount normal recrystallization occurs in heating to the equiaxing temperature. The recent work in the production of single crystals of tungsten and of copper is of interest in this respect, and Edwards and Pfeil⁽¹⁵⁾ have produced enormous grains in carbonless iron, resembling those of Ruder⁽¹⁶⁾ in silicon steel.

Although all of the rules of recrystallization and grain growth are apparently very simple, I have yet to understand just how grain growth actually takes place.

Fig. 1 shows the structure of an ordinary condenser tube heated after the final draw to just the equiaxing temperature, but not held long enough to give complete recrystallization. Numerous new and tiny grains are forming at the old grain boundaries and on the twin planes. Fig. 2 shows the structure of a fine-grained condenser tube. Fig. 3 shows a comparatively coarse one.

Now on heating such annealed and equiaxed material above the last annealing temperature, the grains grow larger. Fig. 4 shows a tube heated for 15 min. at 550° C. Fig. 5 is another piece held for 5 min. at 825° C.

If these grains grow by absorbing their neighbors, why is not growth in geometrical progression instead of by uniformly progressive increase? Is there some kind of reorientation at each maximum temperature, or how must we explain this grain growth?

NEUMANN BANDS

These were first noticed by Neumann in 1848, when studying meteoric iron and were later found by Prestel in commercial iron. Howe dis-



FIG. 1.—ADMIRALTY TUBE, PARTLY RECRYSTALLIZED. $\times 90$.

FIG. 2.—FINE-GRAINED TUBE. $\times 90$.

FIG. 3.—COARSER-GRAINED TUBE. $\times 90$.

FIG. 4.—TUBE REHEATED TO 550°C . $\times 90$.

FIG. 5.—TUBE REHEATED TO 825°C . $\times 90$.

FIGS. 6, 7, AND 8.—NEUMANN BANDS IN SWEDISH WROUGHT-IRON. $\times 90$.
(REDUCED ONE-HALF.)

cusses them at length in his "Metallography of Steel and Cast Iron" (page 415). In 1919 a Committee on the Investigation of Neumann Bands was appointed by the Chairman of the Division of Engineering of the National Research Council with a view to determine if possible the speed of breakage in the metal and to distinguish between fracture caused by an explosion and one caused by an ordinary mechanical strain. In 1922, this work was presented to the Institute in a paper by Foley and Howell⁽¹⁷⁾ entitled "Neumann Bands as Evidence of Action of Explosives on Metals." A further report is to be presented by Foley and Crawshaw at this meeting on "Effect of Air Gap in the Explosion System in the Production of Neumann Bands."

Recently Rosenhain and McMinn⁽¹⁸⁾ read a paper before the Royal Society (March 1925) on the "Plastic Deformation of Iron and the Formation of Neumann Lines." Although the view generally held is that Neumann bands represent areas in which the alpha-iron crystals have become twinned as the result of shock, the authors find that they are really sections of plates or lamellae running through the crystals.

Slip bands were produced in metal containing Neumann bands and were found to cross them in a more or less irregular manner, which seems to prove that the latter are not twins.

Just how much shock is required to produce Neumann bands has not been definitely settled. They have been found in wrought iron after nicking and breaking with a sledge hammer, as well as in the decarbonized surface of forgings and castings after annealing, whose only shock has been that incidental to handling.

The following micrographs are examples of Neumann bands found in Swedish wrought iron, in the neighborhood of the fracture. Fig. 6 is in a bar $\frac{3}{4}$ by $1\frac{5}{8}$ in., Fig. 7 in a bar $\frac{7}{16}$ by 3 in. about $\frac{1}{3}$ in. from fracture, and Fig. 8, in the same near the fracture.

THE DEVELOPMENT OF THE IRON-CARBON DIAGRAM

From Sorby's time we have known that the iron-carbon series was complex. Sauveur's first diagram⁽¹⁹⁾ showed us the relation of ferrite, pearlite and cementite, and Roberts-Austen's diagram⁽²⁰⁾ indicated that with higher carbon content we could have either graphite or cementite as one member of the eutectic. Yet it was well known that cementite and graphite commonly occurred together. In 1900 Rooseboom⁽³⁾ pointed out that such an association could not occur in a system in a state of equilibrium and in order to satisfy the phase rule it was necessary to show a reaction at say 1100° C. between graphite and gamma iron (austenite) to form cementite. On the other hand Stansfield⁽⁴⁾ maintained that at ordinary temperatures ferrite and graphite were the stable phases present. Later Benedicks⁽²¹⁾ summarizing the previous work including that of Heyn⁽²²⁾ and of Charpy⁽²³⁾ proposed a double diagram: (1), the stable,

austenite and graphite; (2) metastable, austenite and cementite. This was an excellent working hypothesis until Goerens⁽²⁴⁾ work showed that all pure cast irons solidified as austenite and cementite and that graphite was the product of the decomposition of cementite and was not an original constituent. Lastly came the work of Wittorf⁽²⁵⁾ showing two new carbides, Fe_4C and FeC_2 . In this connection may be mentioned changes in the diagram proposed by Smits, Hanemann and others, all of which has been discussed by Guertler⁽²⁶⁾ who proposed the new diagram given in Fig. 9.

We have one stable and two metastable diagrams. In the stable diagram, the liquidus is shown by the curves $ABCDE$. Above 1960°C . we have liquid and FeC_2 which resembles graphite in appearance. At

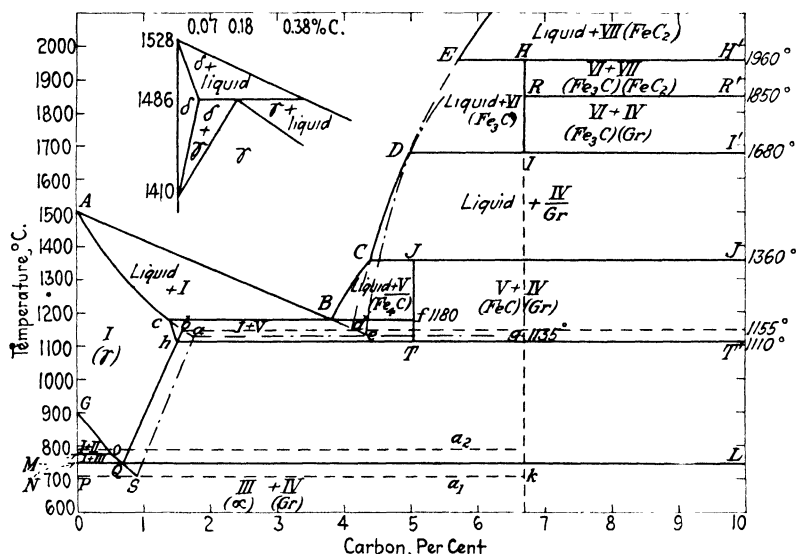


FIG. 9.—IRON-CARBON DIAGRAM (GUERTLER).

1960°C . the FeC_2 reacts with the liquid to form Fe_3C , and at 1850°C . the remaining FeC_2 breaks down into graphite and Fe_3C . At 1680°C . the Fe_3C decomposes and liquid and graphite results. At 1360°C . a reaction between the liquid and the graphite results in the formation of Fe_4C , which forms a eutectic with austenite at 1180°C . and 3.8 per cent. carbon at B. The Fe_4C breaks down into graphite and austenite at 1110°C ., and then at 750°C . we have the eutectoid of ferrite and graphite with 0.7 per cent. carbon, at Q.

The first metastable diagram is produced by suppressing the decomposition of the Fe_3C at 1680°C . and continuing the curve ED to e where at 1135°C . the eutectic of austenite and cementite freezes with 4.3 per cent. carbon, followed by the eutectoid of ferrite and cementite at 0.9 per cent. carbon and 710°C . or the point S. The second metastable

diagram is caused by suppressing the reaction at 1360° C. and continuing the curve *DC* to *d*, which gives the eutectic of graphite and austenite at 1155° C. and 4.1 per cent. carbon, followed by the eutectoid of ferrite and graphite at 750° and 0.7 per cent. carbon as before at *Q*.

Time will not permit discussing the details of this diagram, but it can be said that it explains many of our previous difficulties and harmonizes practically all of the previous work.

Two further points must be mentioned. The first is delta iron, foreshadowed by Ball and proved by Ruer and Klesper.^(26a) In the iron-carbon diagram, at 1486° C. we have the reaction delta 0.07 per cent. C + liquid 0.38 per cent. C = gamma 0.18 per cent. C, as shown by the inset.

The second is the line *MO* showing the transformation of beta into alpha or the magnetic change. Honda's magnetic work⁽²⁷⁾ has shown that the line *MO* should be continued across the diagram as the line *A₂* indicating the magnetic change (maximum) in the whole system and that beta has no place on the diagram.

The application of the X-ray to the study of crystal structure has been most helpful in developing our ideas of the iron-carbon and some of the iron-alloy series. The work of Bain and Jeffries, of Westgren and Phragmen⁽²⁸⁾ may be mentioned in this respect. The crystal lattice of alpha iron is body centered, so is that of beta and of delta iron. Gamma iron, or austenite, has the face-centered lattice. In other words there are only two forms of iron and the beta change is not one of structure and therefore has no place in the diagram. In some of the iron-alloy series the alpha and delta fields are continuous and surround the gamma area.²

Accepting all of these results our iron-carbon diagram still retains its former beauty, but alas, the same cannot be said of the iron-nickel diagram.

THE ALLOYS OF IRON AND NICKEL

These alloys have been studied by the physicists on account of their remarkable physical properties, such as magnetism and coefficient of expansion. At elevated temperatures they form a series of solid solutions but show certain changes with fall of temperature. From the study of meteorites Guertler predicted a eutectoid which was confirmed in the paper of Hanson and Hanson,⁽²⁹⁾ whose diagram is shown in Fig. 10. Now the X-ray shows that the crystal structures of alpha and beta nickel are the same. Hence the curves *PLM* are not a change of phase but merely a magnetic change in the series, and have no place on the diagram.⁽³⁰⁾

² A very clear and readable summary of the present state of X-ray crystallography is given by Zay Jeffries in the report of Sub-committee VI, of Committee E-4 on Metallography, *Proc. Am. Soc. Test. Mat.*, **25**, I (1925).

According to Kasé the magnetic analysis, microscopic and dilatometric examination as well as thermal analysis reduce the diagram to a very simple form and all that is left are the two lines HX and HY , separating the two fields I and II.

MARTENSITE AND THE HARDENING OF STEEL

Probably no subject has caused more discussion than the hardening of steel and the nature of martensite. In 1896, Professor Sauveur read a paper before the Institute on "The Microstructure of Steel and the Current Theories of Hardening," which led to wide interest in and discussion of the subject. The genus metallurgist became divided into two groups, the allotropists and the carbonists, though a few took the

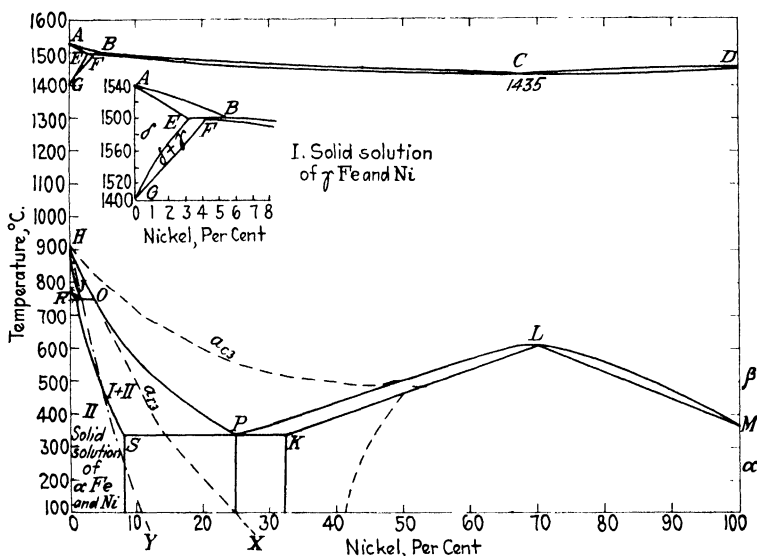


FIG. 10.—IRON-NICKEL DIAGRAM.³

safe course and became carbo-allotropists. With the advent of the amorphous theory of the hardening of metals, and the dawn of our ideas on atomic forces, other theories were developed and the practical man was lost in a maze of contradictions.

The various theories of hardening were most clearly summarized by Professor Sauveur in his "Metallography and Heat Treatment of Steel." He divides them into two main groups:

I. Retention theories, embracing the solution theories, the amorphous iron theory and the carbon theories.

II. The stress theories, which include the early stress theory, inter-strain theory, twinning and amorphous theory.

³ Hanson and Hanson, *Jnl. Iron and Steel Inst.* (1920), II, 39; Hanson and Freeman, *Jnl. Iron and Steel Inst.* (1923), I, 301; T. Kasé, *Sci. Rep. Tohoku I. Univ.* (1925).

Under solution theories, we have two:

Allotropic Theory of Osmond and Roberts-Austen, and later of Howe.—(1) The bulk of the iron passes from the gamma to the beta condition, hence the great hardness produced; (2) some of the beta is transformed to alpha, hence the magnetism; (3) a large proportion of the carbon probably as Fe_3C remains dissolved in the beta iron; (4) the internal pressure created by the transformation of austenite into martensite or gamma into beta may contribute to the final hardness.

Alpha Iron Theory of Le Chatelier and Guillet.—On quick cooling through the critical range, the allotropic transformation from gamma to alpha is not prevented but the steel remains nevertheless in the condition of a solid solution of carbon or Fe_3C in alpha iron, owing its hardness to its state of solution and its magnetism to alpha iron. They consider that the A_2 point is not an allotropic change, and that beta iron does not exist.

The Amorphous Iron Theory of Humfrey.—Hardness is due to the presence of a hard amorphous solution of alpha iron and iron carbide. This is based on the supposition that the passage of a substance from one allotropic modification to another involves the temporary formation of an amorphous state, and if due to sudden cooling, the change point is lowered to a temperature below that at which crystallization in the viscous mass becomes difficult, then the amorphous form will be retained.

The Carbon Theories.—(a) Hardening due to presence of hardening carbon stable only above the critical range; (b) sub-carbide theory of Arnold. Eutectoid steel above its critical point exists as Fe_{24}C , called hardenite.

The Stress Theories.—(a) Hardening due to enforced solution of carbon in iron by sudden cooling (carbonists' theory). Great internal strains result from transformation of austenite to martensite with increased volume, producing hardening similar to that of cold working (A. Le Chatelier, Chary and Grenet). (b) Interstrain theory of McCance: The whole of the carbon remains in solution while the bulk of the gamma is converted into alpha, but owing to the restricted mobility during quenching, the crystalline units are not homogeneously oriented and exist in a condition of inter-strain. (c) Twinning and amorphous theory of Carpenter and Edwards: Quenching produces internal stress and forms numerous twins and hard amorphous layers (martensite).

Now all of these theories were put forth before the end of 1914, and the next advance was the slip interference theory of Jeffries and Archer⁽³¹⁾ in 1921, which explains not only the hardening of metals due to cold work, but also the hardening of steel by quenching. The following summary is taken from the "Science of Metals."

The Essential Points in the Hardening of Steel

Steel owes its hardness fundamentally to the absolute cohesion of the iron atoms.

Pure iron and soft steel are relatively soft and weak because of the presence of crystallographic planes of weakness or potential slip planes in the ferrite grains.

The increased strength and hardness of pearlite, as compared with pure iron are due largely to the increased resistance to slip in the ferrite grains offered by the hard cementite.

The increased hardness of sorbite and troostite, as compared with pearlite, is due to the refinement of the ferrite grains and the greater dispersion of the cementite particles.

The increased hardness of martensite, as compared to troostite and sorbite, is due to a still greater refinement of the ferrite grains and, in cases of maximum hard-

ness, to the critical dispersion of the cementite particles. Carbon in solution or in atomic dispersion in the ferrite makes the ferrite of martensite somewhat harder than the ferrite of pure iron.

The more rapid the cooling of austenite the lower will be the temperature of its transformation into ferrite and cementite. When the transformation takes place at or above the temperature of 600° C., both ferrite and cementite form, yielding pearlite, sorbite or troostite. If the austenite is preserved at a temperature less than about 600° C. it seems to be relatively stable until a temperature of about 300° C. is reached on cooling.

When the austenite transformation is suppressed to about 300 per cent. or lower, the allotropic transformation of iron takes place independently of the carbide formation. Freshly formed martensite therefore, consists essentially of alpha iron in which the carbon is substantially atomically dispersed. Freshly formed martensite is apparently not quite as hard as martensite which has stood at room temperature for several days or has been given a mild tempering treatment.

Carbon is very much less soluble in alpha iron than in gamma iron. The alpha iron of freshly formed martensite contains carbon atoms in atomic dispersion and is therefore saturated with respect to carbon. Equilibrium is brought about only by the precipitation of the carbon in the form of cementite.

Carbon diffuses slowly in alpha iron at room temperature and diffuses more rapidly as the temperature is increased. The carbide therefore precipitates slowly at room temperature and more rapidly with rising temperature.

It is postulated that freshly formed martensite is hard chiefly because of the fineness of the ferrite grains, but partly because the ferrite containing carbon is harder than pure ferrite.

It is postulated that the increase in hardness of freshly quenched martensite on standing at room temperature or after mild tempering is due to the precipitation of cementite, the hard cementite particles "keying" the slip planes of ferrite grains.

Heating tends to soften martensite because it tends to produce growth of the ferrite grains.

Heating produces changes in the carbide which tend to harden the steel until critical dispersion of the carbide particles obtains, and further heating tends to soften.

Growth of the carbide particles is considered to take place as the result of a slight solubility of carbon in alpha iron, which is greater the smaller the size of the cementite particles with which the solution is in contact.

The mechanism of particle growth is such that the matrix, alpha iron, should approximately reach its equilibrium content of carbon before the laws of particle growth begin to apply. This suggests the nearly complete precipitation of the carbide at an early stage of tempering.

Sometimes the composition of the steel is such that rapid quenching preserves austenite at room temperature, whereas moderate rates of cooling do not preserve austenite. The transformation of such austenite into martensite or another product of transformation on aging or tempering results in an increase in hardness. An increase in the hardness of a steel due to this cause is accompanied by an increase in volume.

THE CONSTITUTION OF AUSTENITE, MARTENSITE AND TROOSTITE

The application of X-ray analysis to the study of crystal structure, as well as the recent development of extremely high-power photomicrography notably by Lucas,⁽³²⁾ has tended to upset many of the old theories as to the nature of the constituents of hardened steel.

It is usually granted that austenite is a solid solution of gamma iron, but it is by no means agreed as to the condition of the carbon. Is it in solution as carbon or as iron carbide? Some hold that because carbon diffuses with ease in austenite, it must be in solution as carbon because the carbide is too bulky to pass through the crystal lattice.

What do we mean when we use the term martensite? To many writers martensite refers to the darker needles or the chevrons which occur in a matrix of austenite, while others consider it as the whole complex, chevrons plus matrix.

Again troostite usually forms at the grain boundaries of the austenite with a globular radiating structure. This decomposition product we may call primary troostite. But have we strong enough evidence to prove that it is the same as the secondary troostite which occurs on tempering? Until we have, I think it would help to clarify the discussion if we kept them separate.

It is generally admitted that martensite is alpha iron, but in what form the carbon occurs is still not agreed. Is it carbon or F_3C in solid solution or as a mechanical mixture? One group asserts that it is carbon in atomic dispersion, others that it is F_3C in solution because on tempering F_3C precipitates out, while still others hold that it is Fe_3C in a very fine state of dispersion. Just where a solid solution becomes a mechanical mixture has not been generally decided.

According to Jeffries, fresh martensite is fine-grained ferrite with carbon atomically dispersed. Hardness is due principally to grain refinement but partly to carbon. With aging and slight tempering, Fe_3C forms and the maximum hardness occurs at the critical dispersion of this carbide. To most of us it would appear that the grain size of martensite is often coarse, but Jeffries has explained that his grain size is submicroscopic as indicated by the X-ray, and what we call the martensite grain is really a pseudomorph after austenite. This explains why hardness has little to do with texture, *e. g.*, steels quenched at various temperatures above Ac_3 reach a maximum hardness when the matrix is all fine martensite and generally show a falling off in hardness as the texture coarsens.

According to Matsushita and Honda,⁽¹³⁾ there are really two kinds of martensite, alpha and beta, probably differing in the mode of distribution of the carbon atoms within the space-lattice of the iron atoms. Honda does not admit that martensite is very fine-grained, but accounts for the diffusion of the X-ray spectrum lines by microstrains which alternately increase and decrease the lattice distance.

Whiteley,⁽³⁴⁾ discussing martensite and troostite, distinguishes four types of martensite as the carbon increases in steel: (1) up to 0.6 per cent. C; (2) from 0.60 to 0.75 per cent. C, (3) 0.75 to 1.6 per cent. C and (4) over 1.6 per cent. C. He also distinguishes between two types of troostite A,

the normal kind usually figured in text books, and *M* formed through the breakdown of separate martensite crystallites.

Enlund⁽³⁵⁾ investigated the structure of quenched carbon steels by means of change in electrical resistivity, and specific volume with annealing temperature. He finds that all carbon steels quenched in water in the ordinary way contain some austenite (confirming Westgren and Phragmen's work by X-ray analysis and that martensite in quenched steels is transformed into troostite through annealing at 100 to 200° C., whereas the austenite which is present in all quenched carbon steels does not decompose until it is heated to 200 to 300° C., the reactions being most marked at about 110° C. and 260° C.

From the above all I can conclude is that while the theories of hardening were at wide variance in 1914, the newer theories, based mainly on X-ray analysis and crystal structure and our new knowledge of the structure and plastic deformation of metals, are not all in exact agreement and will not be until we first come to some agreement as to the terms we use and the limits of their meaning.

EXAMPLES OF MARTENSITE AND TROOSTITE

One of the criticisms of so much of our microscopic work on hardened steel is that our samples are all abnormal and are in the nature of freaks. For instance, we are asked what relation there is between an alloy of iron with $2\frac{1}{2}$ per cent. of carbon quenched from 1100° C. in iced brine and a piece of normally hardened tool steel. But martensite and troostite occur in the whole range of steels, not only in tool steels but also in low-carbon steels which are used in everyday practice.

Fig. 11 is a sample from a seamless boiler tube which exploded in a destroyer, $\times 90$. Here we have a martensitic grain of enormous size with fringes of troostite. Fig. 12 shows an area from the head of a marine-boiler rivet which failed, $\times 90$. The rivet was headed by a hydraulic riveter, resulting in an enormous martensitic grain, with typical troostite at the grain boundaries. Fig. 13 shows an area from another rivet head. Typical chevrons of martensite and equally typical troostite, $\times 90$. Fig. 14 is a third example of boiler rivet head. The troostite is now the dominant constituent and thin envelopes of ferrite appear at the grain boundaries, $\times 90$.

Fig. 15 shows the structure of the head of a small deck rivet in which parts of two huge martensitic grains are seen, $\times 90$. Fig. 16 shows part of another grain of the same, $\times 90$.

Such enormous structures are not confined to maltreated low-carbon steels. We find them in tool steels as well.

Fig. 17 is taken from the center of the cutting end of a rock drill and consists of martensite and troostite, $\times 90$. Fig. 18 shows the structure of some of the smaller grains, nearer the outside, $\times 500$. Martensitic

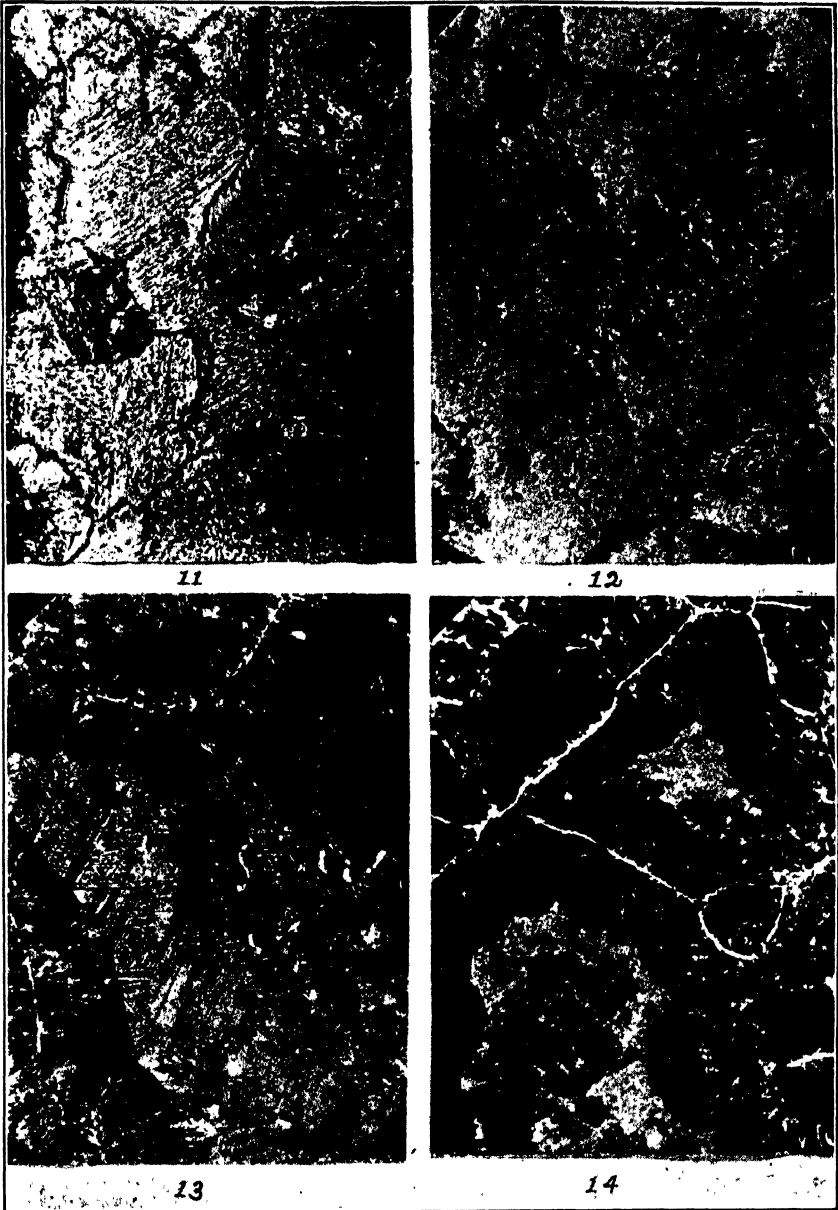
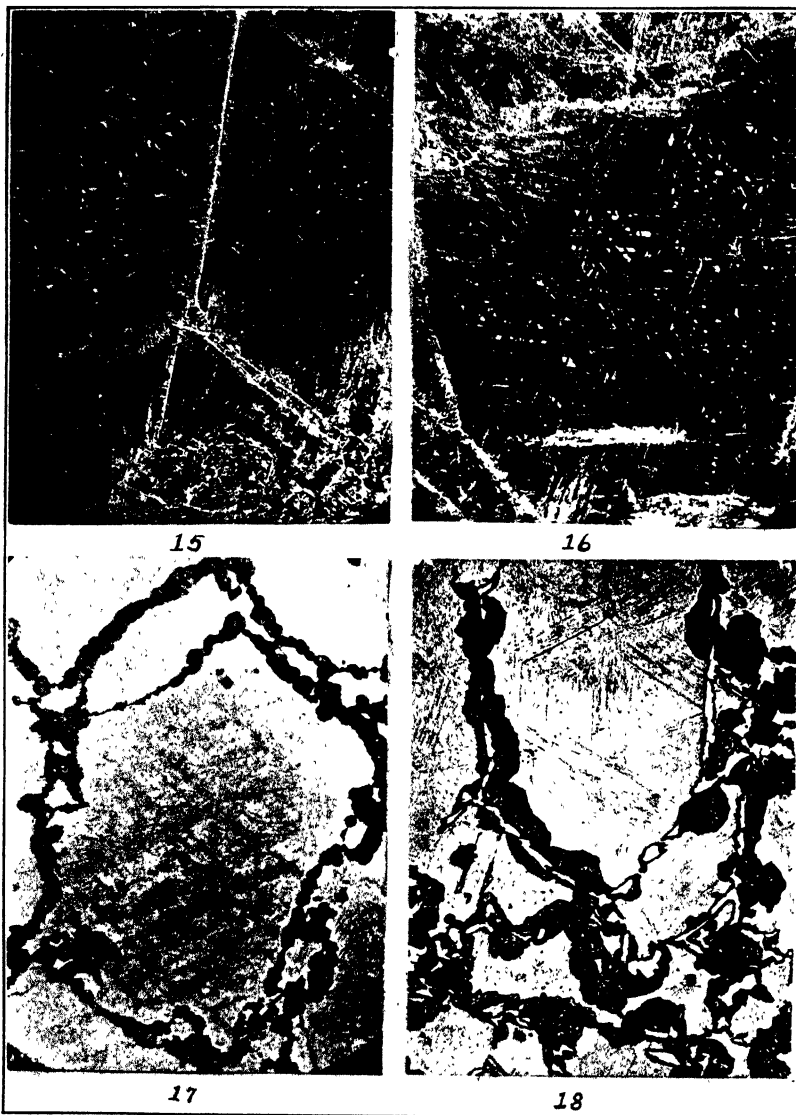


FIG. 11.—BURST BOILER TUBE. MARTENSITE. $\times 90$.
 FIG. 12.—BOILER RIVET. MARTENSITE AND TROOSTITE. $\times 90$.
 FIG. 13.—SAME. MARTENSITE AND TROOSTITE. $\times 90$.
 FIG. 14.—SAME. MARTENSITE, TROOSTITE AND FERRITE. $\times 90$.
 (REDUCED ONE-THIRD.)

grains with typical troostite boundaries and the beginning of the precipitation of ferrite.



FIGS. 15 AND 16.—DECK RIVET. MARTENSITE, TRACE OF FERRITE. $\times 90$.
FIG. 17.—BROKEN ROCK DRILL. MARTENSITE AND TROOSTITE. $\times 90$.
FIG. 18.—SAME. MARTENSITE, TROOSTITE, TRACE OF FERRITE. $\times 500$.
(REDUCED ONE-THIRD.)

IRON AND NITROGEN

The question of the effect of nitrogen on steel has had frequent attention. On the one hand we make nitrogen the scapegoat for the

embrittlement of steel, while others are developing methods of case hardening by nitrogen. Mention may be made of the work of Comstock and Ruder⁽³⁶⁾ in this country and of Fry⁽³⁷⁾ abroad.

The iron-nitrogen diagram was presented by Sawyer⁽³⁸⁾ to the Institute in 1923. Fig. 19 shows a eutectoid at 1.7 per cent. N. and about 610° C. At the eutectoid temperature iron holds 0.1 per cent. N in solid solution but only 0.03 per cent. at normal temperature. The excess precipitates out as nitride needles on cooling. The following illustrations are taken from a very homely source, a failed wrought-iron boiler tube that split in use.

Fig. 20 shows the structure at the inner surface $\times 90$, and resembles ferrite and pearlite. The dark areas however are not the carbide but

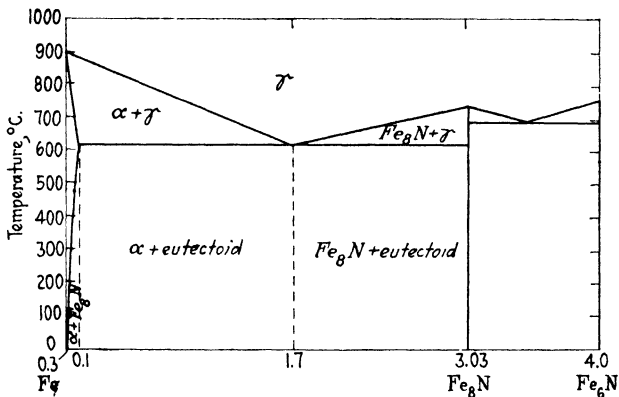


FIG. 19.—IRON-NITROGEN DIAGRAM SHOWING A EUTECTOID AT 1.7 PER CENT. NITROGEN. (SAWYER)

the nitride eutectoid. Fig. 21 is taken from the center, and no longer resembles our usual ferrite and pearlite of low-carbon steel, $\times 90$. Fig. 22 from the outer surface is similar, $\times 90$.

Fig. 23 shows the details of structure which are quite different from pearlite and ferrite, $\times 500$. Fig. 24 shows an area richer in ferrite, $\times 500$.

On heating this material to a cherry red for 30 min., practically all of the nitride disappears.

Fig. 25 shows the center of a strip of tube, one end of which was reheated and the other kept cool; $\times 90$. There is a marked change from Fig. 21, a similar area, and nothing now remains but ferrite and small slag inclusions.

THE STRUCTURE OF ANCIENT ARMOR

Some years ago, my colleague, Dr. Bashford Dean, curator of armor at the Metropolitan Museum, became interested in the structure of old armor. He supplied a number of authentic samples, which were most skillfully mounted and prepared for microscopic examination by Alfred de Forest, who was working in my laboratory at that time. From

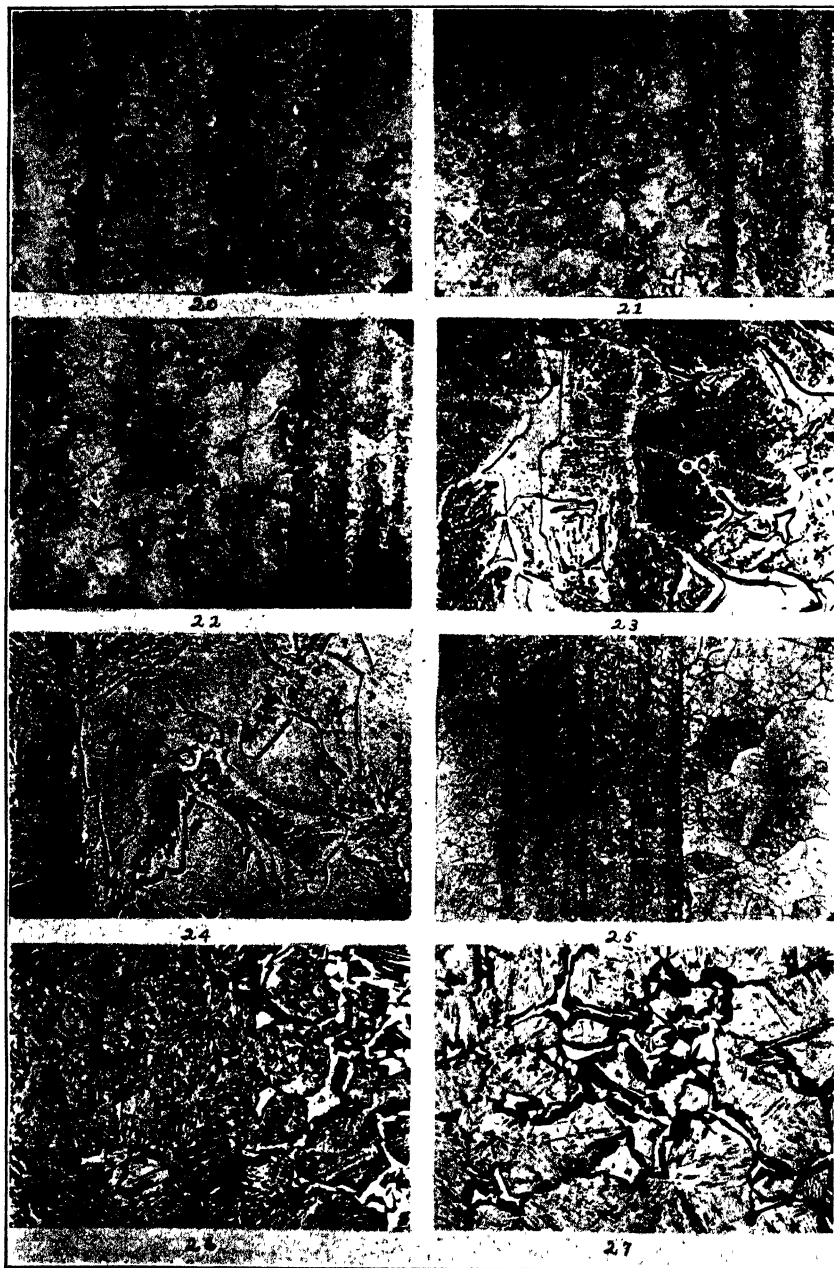
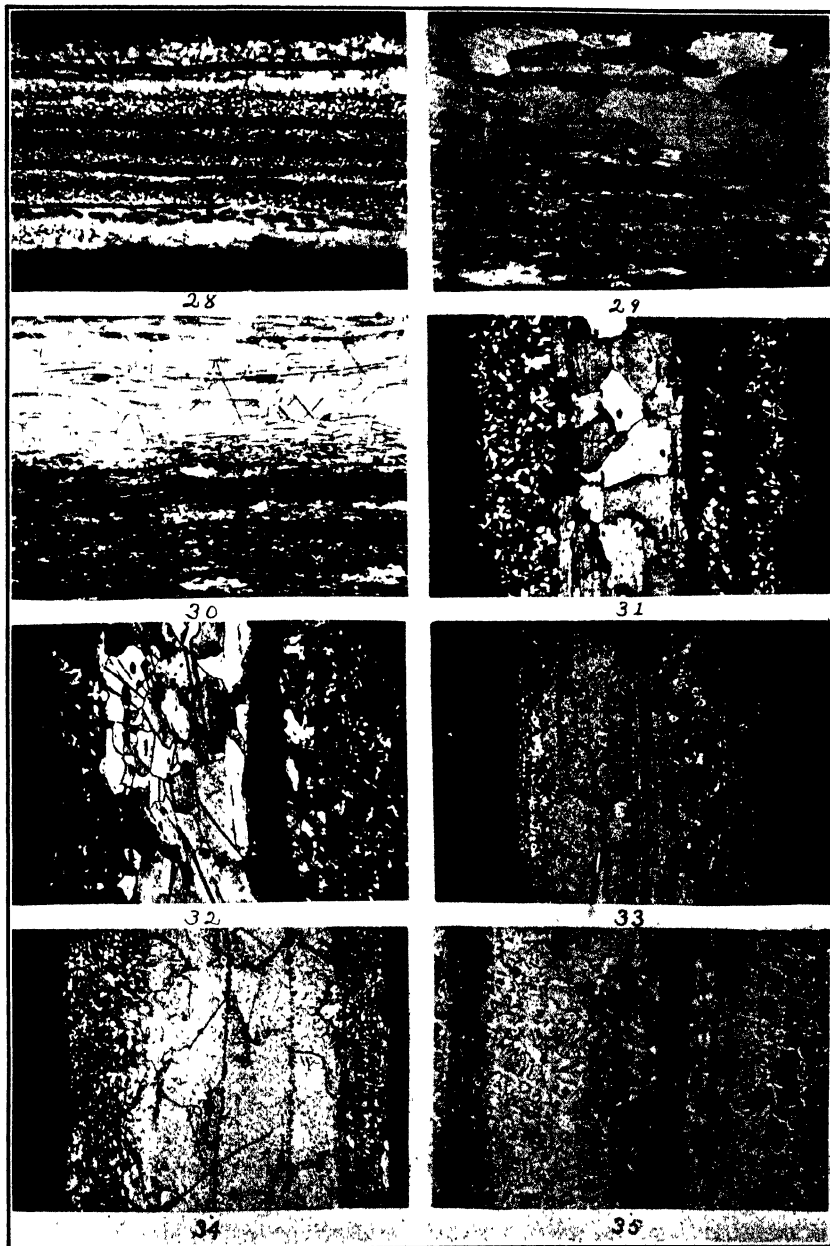


FIG. 20.—BURST BOILER TUBE. INSIDE. $\times 90$.
 FIG. 21.—SAME. CENTER. $\times 90$.
 FIG. 22.—SAME. OUTER SURFACE. $\times 90$.
 FIGS. 23 AND 24.—SAME. $\times 500$.
 FIG. 25.—SAME, HEATED TO CHERRY RED. $\times 90$.
 FIGS. 26 AND 27.—WRIST-PIECE, ABOUT 1460. $\times 450$.
 (REDUCED ONE-HALF.)

FIG. 28.—GERMAN THIGH PLATE, 1500. $\times 90$.FIGS. 29 AND 30.—SHOE, 1515-1525. $\times 90$.FIGS. 31 AND 32.—GOTHIC JAZERAN THROAT PLATE. $\times 90$.FIGS. 33 AND 34.—GERMAN ARM GUARD, 1530. $\times 90$.FIG. 35.—LEG-PIECE, 1580-1600. $\times 90$.

(REDUCED ONE-HALF.)

them I have chosen a few which serve to illustrate the wide variations in structure and which show very beautifully many of our comparatively recent discoveries such as grain growth and germination, Neumann bands and ghosts.

Fig. 26 is a cross-section of a wrist piece, $\times 450$, made by the Missaglia brothers about 1460. This is from the case-hardened outer portion and shows martensite, troostite and ferrite. Fig. 27 shows another area less deeply etched, $\times 450$, with the same constituents.

Fig. 28 is a cross-section from a German thigh-plate dating from 1500, $\times 90$. This is evidently not case hardened but is a natural steel of very

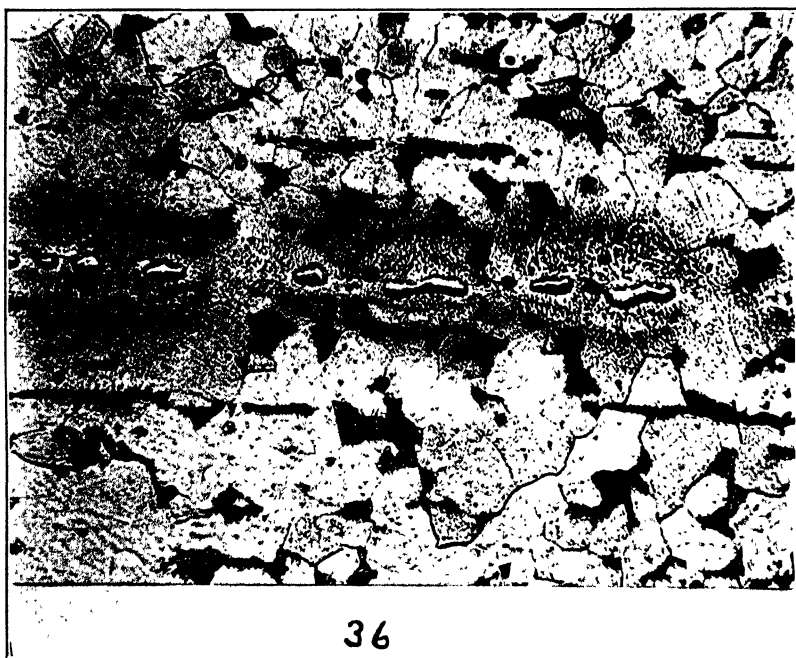


FIG. 36.—ENGLISH SHOULDER PLATE. $\times 450$.

heterogeneous structure. Under a higher power the dark areas are tempered martensite.

Fig. 29 shows a section of a Maximilian shoe of about 1515 to 1525, $\times 90$. Here we have abnormal grain growth or germination as marked as in our laboratory samples. Fig. 30 is another area of the same metal, $\times 90$, etched with 4 per cent. nitric acid in alcohol, which brings out the phosphorus banding in the coarse ferrite area and in addition shows numerous Neumann bands.

Fig. 31, shows a cross-section of a piece of Gothic Jazeran throat plate, $\times 90$, etched with 4 per cent. nitric acid in alcohol. An inner core of

enormous grains of ferrite is shown, with an inner and outer surface of fine grain containing a little carbon.

Fig. 32 is another section, $\times 90$, the coarse grains being full of Neumann bands.

Fig. 33 is a cross-section of a German arm guard of about 1530, $\times 90$. At the surface the grain is extremely fine but the center is very coarse ferrite etching with a peculiar grain boundary similar to that in commercial wrought-iron boiler tubes that have been overheated in service. Fig. 34 is another section of the same, $\times 90$. Here the grains are even coarser and several Neumann bands are seen. Fig. 35 is from a leg piece, 1580-1600, probably English, $\times 90$. The outer surface is carburized but not hardened. The interior is low-carbon with numerous high-phosphorus bands or ghosts, a poor quality of iron judged by our present standards.

Fig. 36 is a piece of English shoulder plate, $\times 450$. The metal is low-carbon and has a typical ghost or high-phosphorus band through the center. The phosphorus is so high as to produce the light elongated globules in the center, a condition rarely met with today even in the poorest samples of screw stock.

An examination of this old armor makes us discount our old ideas about superlative quality and at the same time increases our admiration for the workmanship, for the armorer must have had great skill to produce the intricate shapes out of such poor material. Furthermore the frequent occurrence of Neumann bands leads to some speculation as to the hard knocks the wearer had to put up with.

MARTENSITIC STRUCTURE IN NON-FERROUS ALLOYS

It often happens that the reputation of a man is built on one phase of his work, while his other interests in time are forgotten. This is so with Professor Howe, of whom we are beginning to think in terms of his work in the "Metallography of Iron and Steel." We forget his early work as a practical copper metallurgist. When I came to Columbia I found he was keenly interested in the copper alloys. One experiment I particularly remember was making diffusion alloys of copper and aluminum and examining their structure. Dr. Matthews and I had already played with this series in London. It was found that at the copper end they resembled the bronzes showing two phases alpha and gamma with a eutectoid between. They were peculiar in this respect, that the eutectoid only developed on slow cooling, whereas when cooled in air and when quenched martensitic beta was preserved.

Fig. 37 shows one of these early diffusion alloys, cooled in air, $\times 33$. In the lower part we have the dendrites of alpha passing up into martensitic beta. In the upper part dark etching dendrites of gamma grow down into the beta. On annealing the beta is replaced by a pearlitic eutectoid.

The resemblance of this series to the ferrite-cementite series was noted in the "Progress of Metallography for 1902" in *Mineral Industry* and illustrated by micrographs of air-cooled, quenched and tempered samples.

The effect of rate of cooling on the hardness of these alloys and their constitution is shown in Fig. 38. The maximum at $10\frac{1}{3}$ per cent. Al and minimum at $12\frac{1}{4}$ per cent. Al are very striking. The constitutional diagram⁽³⁹⁾ shows that alpha is saturated at 10 per cent. Al, that from 10 to $12\frac{1}{4}$ per cent. Al we have alpha grains in increasing amounts of eutectoid

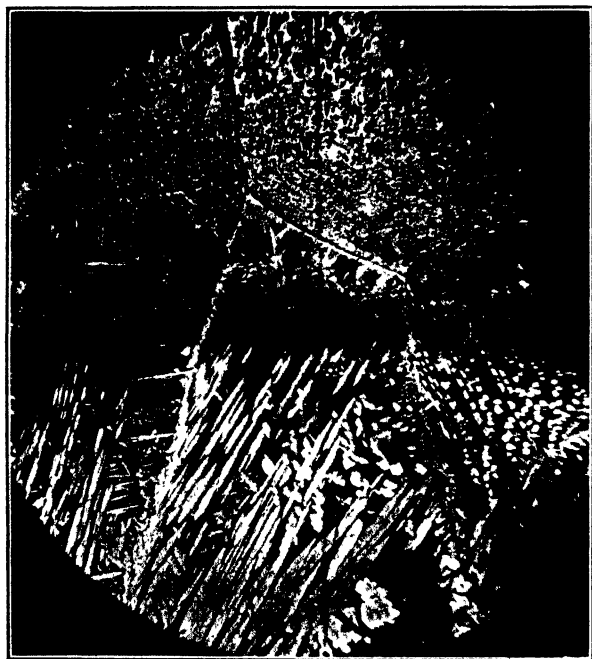


FIG. 37.—A DIFFUSION ALLOY OF COPPER AND ALUMINUM, COOLED IN AIR. $\times 33$.

when slowly cooled and that from $12\frac{1}{4}$ per cent. Al up to 16 per cent. the gamma increases and the eutectoid decreases.

The dotted line *bv* is the boundary of the cored alpha in sand-cast alloys and the dotted horizontal *vw* is the eutectoid-beta change in ordinary heating say at 560°C . The effect of the rate of cooling and the occurrence of martensite is well shown in the following illustrations.

Fig. 39 is an alloy containing 10.2 per cent. Al., a 50-gm. melt cooled in the crucible, $\times 450$. It consists of alpha grains in a matrix of martensitic beta. On slow cooling in the furnace or on annealing just below the eutectoid line the beta breaks up into the eutectoid of alpha and gamma. Quenched from 900°C . the structure is entirely martensitic as in Fig. 41 and the hardness is more than doubled.

Fig. 40 shows an alloy with 11.6 per cent. Al annealed at 800° C. and slowly cooled in the furnace, $\times 90$. It is almost of eutectoid composition as there is only a small amount of white alpha rods and grains present. The matrix resembles pearlite and is composed of fine plates of gamma in alpha. Fig. 41 is the same alloy quenched from 700° C. and is martensitic beta, $\times 90$. The hardness is about the same as that of the furnace-cooled alloy.

Fig. 42 shows the structure of a 50-gm. melt cooled in the crucible in air, $\times 450$. The junction of three martensitic grains are seen with a small amount of alpha precipitating at the grain boundaries.

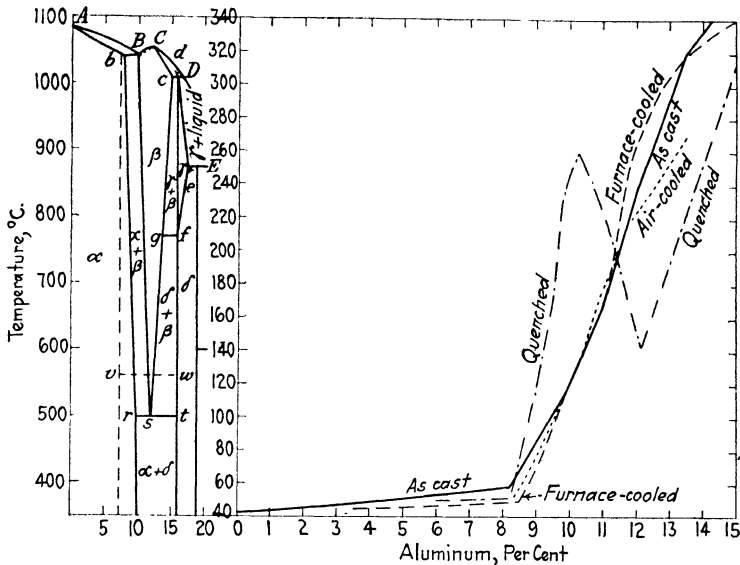


FIG. 38.—ALUMINUM BRONZE DIAGRAM. BRINELL HARDNESS, ANNEALED AT 900° C., AND COOLED IN DIFFERENT WAYS.

The variation in hardness of these quenched alloys with the aluminum content is apparently anomalous unless we explain it by the slip interference theory and say that at $10\frac{1}{4}$ per cent. Al we have maximum interference to slip due to critical dispersion of gamma in the martensitic structure. Beyond this point the gamma becomes coarser and coarser, and in spite of the increase in amount there is less interference to slip. Beyond $12\frac{1}{4}$ per cent. Al, it is the actual hardness of the gamma that causes increase in hardness.

Comstock and Corse⁽⁴⁰⁾ have shown that the 10 per cent. aluminum bronze is markedly improved by the addition of 1 per cent. of iron. Further improvements can be made by small amounts of nickel, manganese, etc., as in the case of manganese bronze. These improvements are very marked in alloys after quenching and tempering as the figures in Tables 1, 2 and 3 show.

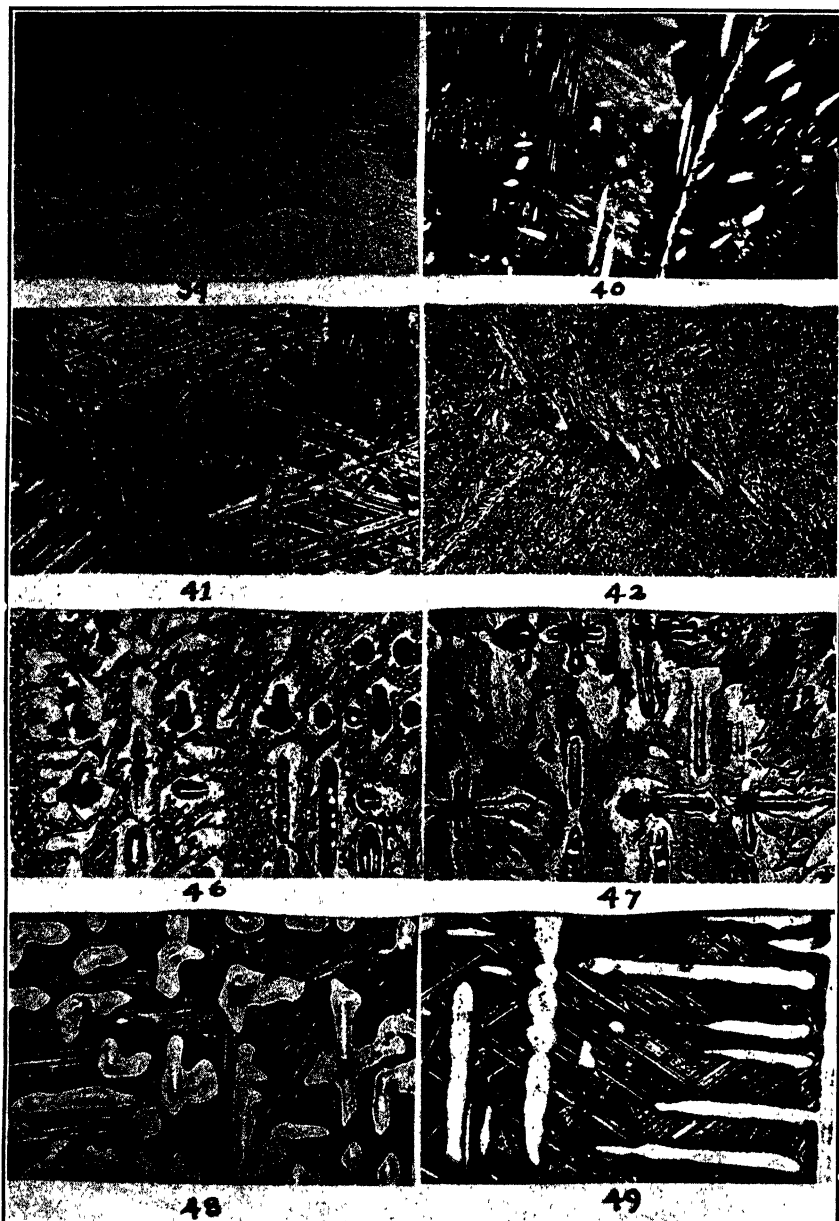


FIG. 39.—10.2 PER CENT. AL, AIR-COOLED, MARTENSITIC MATRIX. $\times 450$.

FIG. 40.—11.6 PER CENT. AL, FURNACE-COOLED FROM 800°C ., PEARLITIC. $\times 90$.

FIG. 41.—SAME, QUENCHED FROM 700°C . MARTENSITIC. $\times 90$.

FIG. 42.—SAME, AIR COOLED, MARTENSITIC. $\times 450$.

FIG. 46.—Cu 80 PER CENT., Sn 20 PER CENT. CHILL-CAST; ALPHA AND EUTECTOID. $\times 500$.

FIG. 47.—SAME. ALPHA AND BETA. $\times 500$.

FIGS. 48 AND 49.—ALPHA AND MARTENSITIC BETA. $\times 500$.

(REDUCED ONE-THIRD.)

The alloys were cast centrifugally and the cylinders cut and flattened hot and then the test pieces were machined out. Unfortunately, the threaded portions of the test bars had very sharp threads and several bars broke in the grips. However, there are enough figures to show what can be expected of this material, which has a remarkable resistance wear. Structurally the first alloy resembles that shown in Fig. 39 while the second and third are like Fig. 42, when air-cooled or quenched and tempered.

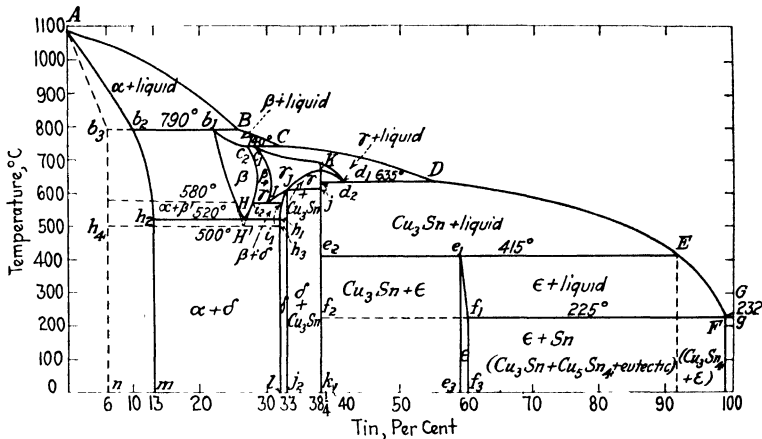


FIG. 43.—COPPER-TIN DIAGRAM (1915).

TABLE 1.—Centrifugal Cast No. 1

(Cu 89.45 per cent., Al 9.75 per cent., Fe 0.93 per cent.)

CBX	Treatment	T. S., Lb. per Sq. In.	Yd. Pt., Lb. per Sq. In.	El. 2 In., Per Cent.	R. A., Per Cent.	Brinell, 1000 Kg.
48-1	As cast.	66,550	26,900	35.0	36.0	97.6
53-3	Quench at 850° C. Draw at 445° C., 30 min.	62,000	36,300	8.5	11.1	129
53-2	Quench at 850° C. Draw at 610° C., 15 min.	65,000	31,600	24.5	25.2	107
53-1	Quench at 850° C. Draw at 650° C., 15 min.	63,600	31,950	24.0	25.2	107
53-4	Forge at 675° C. Quench at 675° C.	86,250	34,200	14.5	16.3	153.4
61-1	As cast.	68,700	25,450	36.5	35.3	97.6
-2	Quench at 800° C.	71,500	36,350	13.0	21.3	134
-3	68,700	34,500	13.0	19.6	139.4
-6	Quench at 800° C. Draw at 310° C., 30 min.	71,800	37,600	11.5	17.8	143.4
-7	72,900	32,400	10.5	16.7	139.4
-8	Quench at 800° C. Draw at 400° C., 30 min.	69,200	34,400	8.5	14.5	139.4
-9	72,000	32,900	8.25	13.0	139.4
-10	Quench at 800° C. Draw at 500° C., 30 min.	63,800	39,100	8.0	11.1	121.4
-11	69,800	36,800	10.0	12.2	121.4
-4	Slow from 900° C.	52,500	27,850	18.0	18.5	89.6
-5	51,100	27,550	24.9	16.2	89.6

TABLE 2.—*Centrifugal Cast No. 2*

(Cu 81.49 per cent., Al 10.68 per cent., Fe 4.25 per cent., Ni 3.58 per cent.)

CBX	Treatment	T. S., Lb. per Sq. In.	Yd. Pt., Lb. per Sq. In.	El., 2 In., Per Cent.	R. A., Per Cent.	Brinell, 1000 Kg.
49-1	As cast.....	92,100	40,150	5.0	6.6	192 6
62-1	As cast.....	99,900	60,800	5.5	7.0	200
-2	800° C., 20 min. and quench.....	71,700	62,700	1.5	2 3	248
-3	800° C., 20 min. and quench.....	70,800	61,200	2 0	2 0	248
-6	800 °C., draw 310° C., 30 min.....	104,700	69,900	1.0	0 4	286
-7	800° C., draw 310° C., 30 min.....	100,800	72,500	1.0	1.5	272
-8	800° C., draw 400° C., 30 min.....	97,000				
-9	800° C., draw 400° C., 30 min.....	101,540				316
-10	800° C., draw 500° C., 30 min.....	119,250				300
-11	800° C., draw 500° C., 30 min.....	116,720				
-4	800° C., furnace cool.....	80,300	55,400	3.0	4 3	165
-5	800° C., furnace cool.....	75,200	50,400	2.0	3.8	165
54-3	Quench at 850° C. Draw at 445° C., 30 min.	66,800	31,100	0 0	0 8	286
-2	Quench at 850° C. Draw at 610° C., 15 min.	93,500	63,150	4.0	6.6	200
-1	Quench at 850° C. Draw at 650° C., 15 min.	104,650	32,650	5.0	6.6	281

NOTE: Samples 8, 9, 10 and 11 broke in the threaded part of the test pieces. The broken pieces were turned down to smaller size and again pulled. Nos. 8 and 9 again broke in the threads at the load given in the table. Nos. 10 and 11 broke in the reduced section which however was too small to determine the yield point or elongation.

TABLE 3.—*Centrifugal Cast No. 3*

(Cu 79.01 per cent., Al 10.54 per cent., Fe 3.09 per cent., Mn 1.62 per cent., Ni 3.64 per cent.)

CBX	Treatment	T. S., Lb. per Sq.]	Yd. Pt., Lb. per Sq.]	El., 2 In., Per Cent.	R. A., Per Cent.	Brinell, 1000 Kg.
51-1	As cast.....	94,500	37,350	11.0	11.1	165
52	Forged at 675° C., then quenched at 675° C.	106,800	41,900	6.5	9 5	185
63-1	As cast.....	95,100	51,800	10.5	13.7	159
-2	800° C., 21 min. Quench.....	94,000	51,700	5.0	9 7	170.6
-3	800° C.....	102,900	57,200	8.0	10.5	170.6
-6	800° C., draw 310° C., 30 min.....	101,800	45,000	8.0	10.4	170
-7	800° C., draw 310° C., 30 min.....	101,800	42,600	8.0	9.7	170
-8	800° C., draw 400° C., 30 min.....	99,600	48,800	5.5	7.0	185
-9	800° C., draw 400° C., 30 min.....	94,900	50,200	5.0	9.0	170
-10	800° C., draw 500° C., 30 min.....	99,700	50,200	7.5	7.8	177.4
-11	800° C., draw 500° C., 30 min.....	99,200	51,200	8.5	10.7	170.5
-4	800° C., and furnace cool.....	84,800	53,700	7.0	11.6	159
-5	800° C., and furnace cool.....	90,600	51,200	8.5	10.8	159

PROGRESS IN OUR KNOWLEDGE OF THE CONSTITUTION OF ALLOYS

Twenty-five years ago our knowledge of the constitution of alloys was confined to microstructure and one or two simple curves. Of the complex series such as the brasses and the bronzes we had only the liquidus curves of Roberts-Austen and Stansfield. The liquidus and the transformations in the solid had not been determined until the remarkable paper on the copper-tin series by Heycock and Neville.⁽⁴¹⁾ This work gave a new impetus to the study of the constitution of alloys in general.

Having determined the liquidus and solidus for various systems, some of the more painstaking workers turned their attention to the accurate determination of the solubility curves in the solid state, and the results marked a further advance in our knowledge. As an example of this, I might mention the solubility curve of CuAl_2 in Al, from which Merica⁽⁴²⁾ and his associates explained the hardening of duraluminum, a marked advance along the road to the slip interference theory of hardness.

As an example of the constant changes in constitutional diagrams made necessary by new work we have only to consider the copper-tin series.

In October, 1899, the author started work in Roberts-Austen's laboratory at the Royal School of Mines with a view to explain the complete freezing-point curve of the copper-tin alloys of Roberts-Austen and Stanfield, published in the Fourth Report of the Alloys Research Committee, and to note the change of structure due to casting and rapid cooling. The results of this work were published in December, 1901, as an appendix to the Reports of the Alloys Research Committee,⁽⁴³⁾ and appear very crude alongside those of Heycock and Neville.⁽⁴¹⁾ They did, however, show the existence of the eutectoid at about 26 per cent. of tin and of a second eutectoid structure in the alloys around 34 per cent. of tin.

And here I would like to pay tribute to two kindly gentlemen, for when Heycock and Neville discussed the paper at the meeting, they said they were very much interested in the paper because it showed that two sets of workers had been going over the same ground quite independently and simultaneously, and wherever their experimental methods were comparable they seemed to have obtained the same results, but they had taken advantage of the theory of Prof. Bakhins Rooseboom, concerning the manner in which complexes solidified when they formed solid solutions, and by means of that theory they were able to state the results in a form which, though still difficult, was perhaps a little easier to grasp. They could just as easily have said that I knew nothing about the physical chemistry of solutions and therefore could not interpret the results I obtained, which would have been no more than the truth. We sometimes forget that such kindly interest is like manna from heaven to the young beginner who needs all the encouragement we can give him.

Just as Roberts-Austen's diagram settled once for all the liquidus curve, so the Heycock and Neville diagram forms the basis of the solidus and changes in the solid.

In 1906, Shepherd and Blough⁽⁴⁴⁾ who had been working under Bancroft, published their diagram and explained the horizontal or the solidus at 740° C. which Heycock and Neville left in doubt. Furthermore they placed a new eutectoid at about 575° C., when gamma breaks up into beta and delta.

Corey⁽⁴⁵⁾ in 1915 worked on the limits of the beta + gamma field and the transformation of gamma into beta + delta. In 1913 Hoyt,⁽⁴⁶⁾ continuing with Hanemann and Guertler, work started at Columbia, found a transformation in the alpha + beta field at 590° C. This has been explained in three different ways. Bauer and Vollenbruck⁽⁴⁷⁾ show it as a eutectoid of alpha and gamma, Stockdale,⁽⁴⁸⁾ 1925, as a transformation in the beta itself, while Isihara⁽⁴⁹⁾ shows it as a transformation in the alpha.

Fig. 43 is the diagram of 1915, showing the two eutectoid changes at *H* and *I*, and the limit of the alpha field at *Ab₂h₂m*. For alloys cooled in

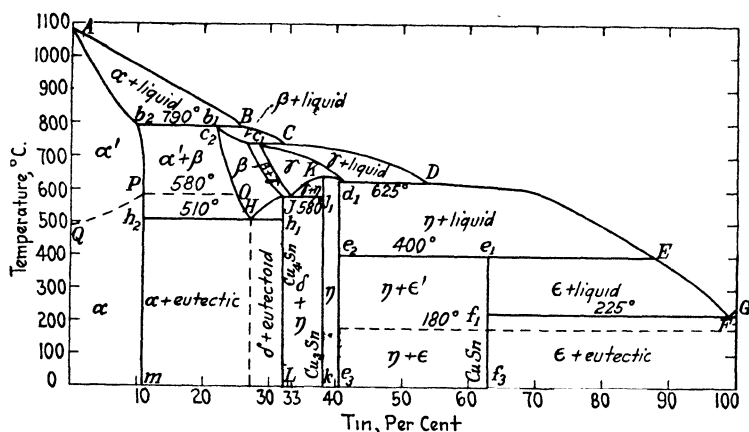


FIG. 44.—COPPER-TIN DIAGRAM.⁴

air or sand castings, the lower eutectoid is given to the broken line and the boundary of the alpha field (unsaturated) by the line for beyond this the eutectoid is found in castings. Isihara's diagram, Fig. 44, shows the heat effect at 580° C. as a transformation in the alpha. Another remarkable point about this diagram is the breakdown of gamma into a eutectoid at 580° C.

Stockdale in 1925 found the point *b₂* at 13.3 per cent. Sn and 799° C., the eutectoid *h₂Hh₁*, at 518° C. and the saturation point of alpha at 16 per cent. Sn. The change at 590° C. is due to a polymorphic transformation in the beta phase. Fig. 45 shows Bauer and Vollenbruck's diagram to which have been added Stockdale's alpha boundary as well as Houghton's⁽⁵⁰⁾ (1921) results on the tin-rich side.

Comparing these diagrams there are two main points of difference: First, the transformation in the alpha + beta field at 590° C. may be (a)

⁴ T. Isihara, 1924.

a polymorphic change in the alpha; (b), a polymorphic change in the beta; (c), the transformation of beta into a eutectoid of alpha and gamma. Second, the directional change of the beta + gamma field. In the older diagrams the gamma breaks up into a eutectoid of beta and delta (I, Fig. 43). This is missing from the two later ones and, (a), beta breaks up into a eutectoid of alpha and gamma (R, Fig. 45) or, (b), gamma breaks down into delta + eta (Fig. 44).

Several years ago an attempt was made to settle the beta change by taking a small chill casting about 2 in. long containing 20 per cent. Sn and heating one end to the melting point while the other was held in water, and then quenching. The piece was polished and etched with ammonia and peroxide and then stained with Grard's solution (ferric chloride).

Fig. 46 shows the structure of the metal up to the lower change point (518° C.) and consists of cored alpha in matrix of fine eutectoid of alpha and delta, $\times 500$.

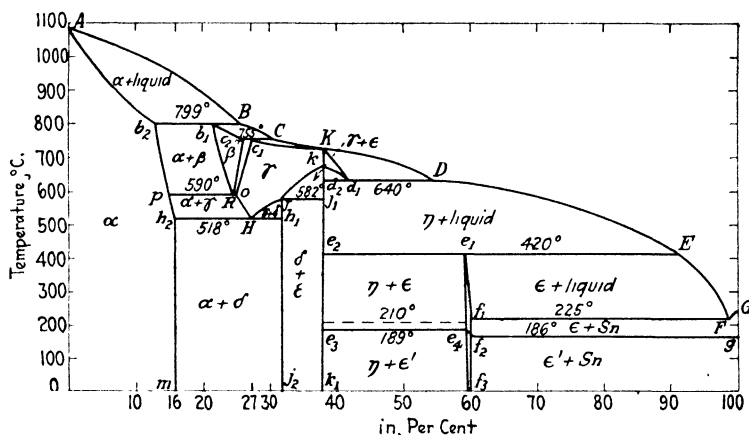


FIG. 45.—COPPER-TIN DIAGRAM.⁵

Fig. 47 shows the structure of the metal quenched in the range 518 to 590° C., cored alpha in a plain beta matrix. Fig. 48 shows the metal quenched above 590° C. alpha in a matrix of martensitic beta, and in Fig. 49, metal heated to near the melting point, much of the alpha has gone into solution and the beta is now strongly martensitic.

If, however, the same experiment is performed on metal with a coarser structure is used, the transformation at 518° C. is not as sharp. A piece of slowly cooled metal of 20 per cent. Sn was heated differentially and quenched as before. Fig. 50 shows the structure of the original metal, alpha grains in a matrix of coarse eutectoid. Fig. 51 shows the area heated to just over the lower transformation point. Much of the delta remains unabsorbed and the matrix is now a mixture of beta and delta. In Fig. 52, the metal was heated somewhat hotter and now only the coarsest of the delta remains unabsorbed. Fig. 53 shows the change practically complete and the matrix is beta. There is no sign of a eutectoid structure. Fig. 54 was heated above the 590° C. change and the beta is now martensitic; in Fig. 55 the metal reached

⁵ Hoyt. *Jnl. Inst. Metals* (1913), X, 225; Bauer and Vollenbruck. *Ztschr. f. Metallkunde*, 25, 119; Stockdale. *Jnl. Inst. Met.* (1925), II; Haughton. *Jnl. Inst. Met.* (1918), I, 222 (1921), I, 309.



FIG. 50.—Cu 80 PER CENT., Sn 20 PER CENT. SAND-CAST; ALPHA AND EUTECTOID. $\times 500$.

FIGS. 51 AND 52.—SAME; ALPHA, BETA AND DELTA. $\times 500$.

FIG. 53.—SAME; ALPHA AND BETA. $\times 500$.

FIGS. 54 AND 55.—ALPHA AND MARTENSITIC BETA. $\times 500$.

FIG. 56.—Cu 65 PER CENT., Sn 35 PER CENT.; DELTA AND "EUTECTOID." $\times 90$.

FIG. 57.—SAME; DELTA, "EUTECTOID" AND Cu₃Sn. $\times 90$.

(REDUCED ONE-THIRD.)

the neighborhood of 799° C. and much alpha was absorbed by the beta which is still martensitic.

The above seems to confirm the idea that the heat effect at 590° C. is due to a transformation in the beta (which is martensitic when quenched above 590° C.), but why is it confined to the alpha + beta field?

The second point of difference is more difficult to unravel. That a eutectoid-like structure occurs around 34 to 35 per cent. Sn has been known since 1900. Yet Ishihara is the first to show such a change in the diagram, all previous ones making gamma precipitate eta until it reached the composition 31.8 per cent. Sn when it transformed into delta or Cu_3Sn . The following figures illustrate the occurrence of the eutectoid structure.

Fig. 56 shows an alloy containing 35 per cent. Sn annealed and slowly cooled in the furnace, $\times 90$. The light areas are delta, or Cu_3Sn , in which are patches with a pearlitic or eutectoid structure.

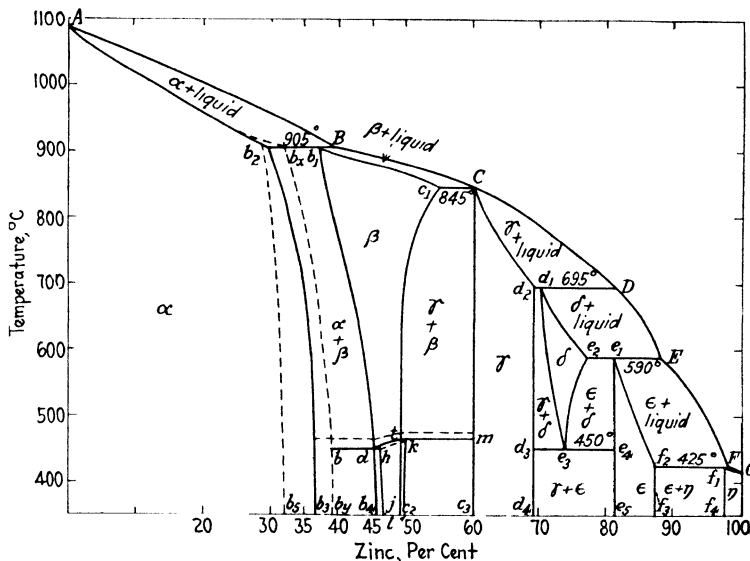


FIG. 58.—COPPER-ZINC DIAGRAM.*

Fig. 57 shows another area containing light areas of delta or Cu_3Sn , dark patches of eta or $\text{Cu}_{11}\text{Sn}_4$ with only a few small areas with the eutectoid structure, $\times 90$. According to Ishihara's diagram this alloy ought to consist of Cu_3Sn or eta and eutectoid. Until further evidence is produced we must accept the older diagrams as correct.

To settle these questionable eutectoid points, a diffusion alloy about 2 in. high and 2 in. wide was prepared so that the composition varied from pure copper at the bottom to 38 per cent. Sn at the top, and a thin section cut out. One side was heated to the melting point while the other was held in water in order to show in one piece all of the transformations up to 38 per cent. Sn. Unfortunately the corner corresponding to 30 to 38 per cent. Sn and from say 600° C. to the liquidus, broke up into small pieces on quenching and these could not be fitted together again. Imperfect as this was there was evidence that the eutectoid occurred at I . As soon as time permits this will be repeated, first mounting the specimen in a frame to prevent shattering on quenching.

* Shepherd, 1904; Mathewson, 1917; Genders and Bailey ($b_x b_y$), and Gayler ($b d h t k m$), 1925.

The Brasses

To Roberts-Austen and Stansfield⁽⁵¹⁾ we owe the liquidus curves. In 1904 Shepherd's diagram⁽⁵²⁾ showed the transformations in the solid, and the limits of the various fields. In Fig. 58 the line b_2b_3 is the solubility curve of beta in alpha, while b_1b_4 and c_1c_2 are the limits of the beta field. Roberts-Austen and Stanfield found a heat effect in the alpha + beta field about 450° C. which Shepherd could not confirm.

Carpenter and Edwards⁽⁵³⁾ in 1911 however found this transformation extending from the alpha to the gamma boundary and interpreted it as a breakdown of the beta into a eutectoid of alpha and gamma.

In 1917, Mathewson and Davidson⁽⁵⁴⁾ redetermined the beta field boundaries and showed that the heat effect at 450° C. was a transformation in the beta.

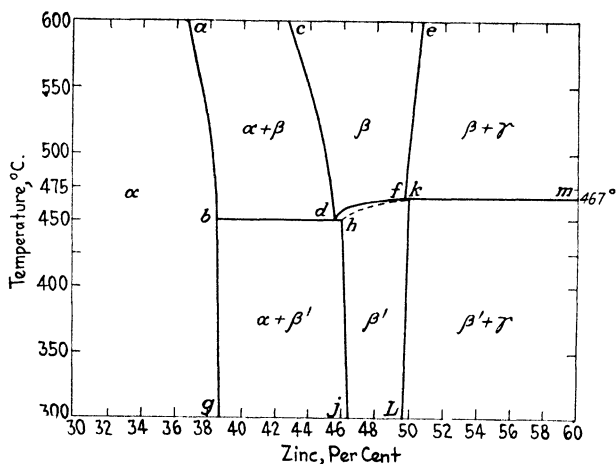


FIG. 59.—THE BRASSES, TRANSFORMATION IN BETA (GAYLER).

Until recently 36½ per cent. Zn has been taken as the solubility of zinc in copper or the limit of alpha, as shown in Fig. 58 where b_2b_3 is drawn to indicate the boundary between the alpha and the alpha + beta fields in castings.

In 1925, Genders and Bailey⁽⁵⁵⁾ redetermined this boundary and showed the limit was 39 per cent. Zn, while Marie Gayler⁽⁵⁶⁾ redetermined the beta field and the transformation temperature in the beta (Fig. 59). Thus the brasses being less complex than the bronzes have been satisfactorily explained by the thermal diagram.

Unfortunately, however, Westgren and Phragmen,⁽⁵⁷⁾ 1925, have found by X-ray analysis that the thermal effect in the beta at 450° C. is very probably not a polymorphic change, neither is it a breakdown into alpha + gamma, so that for the present its meaning must be left in doubt.

The Ternary Diagram of Copper with Zinc and

Due to the fact that so many brasses contain tin and numerous cast bronzes contain more or less zinc, a knowledge of their constitution is important. With the changes in the CuSn and the CuZn diagrams in respect to the saturation points for alpha similar changes must be made in the ternary diagram shown in Fig. 60. Here the alpha + beta field corresponds to the Muntz metal type of alloys, and the alpha + eutectoid field represents the gun metal type. Between the two is a field in which the alloys consist of alpha + beta + eutectoid or alpha + beta + gamma. It is probable, however, that this is not in a state of equilibrium

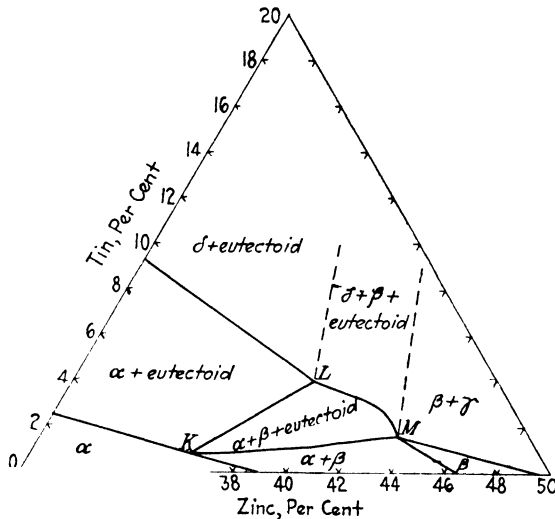


FIG. 60.—COPPER-ZINC-TIN DIAGRAM.

	COPPER PER CENT.	ZINC PER CENT.	TIN PER CENT.
K.	53.2	36.0	0.8
L.	57.0	39.0	4.0
M.	55.0	43.4	1.6

because it was determined by annealing above the temperature at which the eutectoid change occurs followed by slow cooling. To arrive at true limits determinations will have to be made on small chill cast ingots quenched and then annealed for a long time just below the transformation points in order to ensure the complete breakdown of the beta.

Causes of Failure in Brasses and Bronzes

One of the serious troubles that have been encountered in the past has been the mysterious cracking and failure of cold-worked brass containing over 25 per cent. Zn. This so-called season cracking was discussed in 1914 by Heyn⁽⁵⁹⁾ and very thoroughly in 1918 by various authorities,⁽⁶⁰⁾ especially that phase relating to cartridge brass, and is now

no longer a mystery. But in the cast bronzes and brasses we still encounter troubles such as porosity, shrinkage cavities, intergranular films and weakness, which are all below the surface. The usual specification for gun metal (88Cu.10Sn.2Zn) calls for 30,000 lb. per square inch tensile strength in a sand-cast test-bar and yet 50,000 lb. with 30 per cent. elongation in 2 in. is not unknown in well-poured metal.

Fig. 61 shows a section cut from a gun metal casting with a tensile strength of 37,650 lb. per square inch and 16 per cent. elongation in 2 in., $\times 450$. It consists of cored alpha with small evenly distributed patches of the eutectoid surrounded by saturated alpha. The cores of the alpha are full of slipbands, because the specimen was cut from the threaded end of the test-bar.

Fig. 62 shows an area in a piece with 22,900 lb. per square inch tensile strength and 4 per cent. elongation, $\times 450$. At the grain boundaries are films and partings which account for the poor physical properties. Such a test-bar has a dull reddish-gray fracture and the explanation usually given is that the metal is oxidized and due to poor melting. Now the oxide formed in poor melting is SnO_2 as Heyn⁽⁶¹⁾ showed many years ago, because the Cu_2O formed in melting the copper is reduced by the addition of tin. The tin oxide formed occurs in small grains or crystals and is comparatively harmless. That such is so can easily be demonstrated. If copper is melted in air so as to be well oxidized and tin or bronze is then added, the alloy will show numerous distinct crystals or grains of SnO_2 .

Fig. 63 is a piece of an alloy made from oxidized copper (melted in air) and 15 per cent. Sn added after melting, $\times 90$. The dark crystals are oxide of tin which show no tendency to form films. Fig. 64 is part of a diffusion alloy made by melting copper in air and pouring on top an alloy with 20 per cent. Sn, $\times 400$. The matrix is a bronze corresponding to about 10 per cent. Sn whereas the oxide occurs in tiny grainstand not as films.

Rawdon⁽⁶²⁾ and Comstock⁽⁶³⁾ have both discussed this subject at length, and we must conclude that oxides as such are relatively unimportant and that dendritic shrinkage cavities and films or partings are the main cause of failure.

Effect of Heat-treatment in Alloys

Very little work of any practical importance was done on the heat treatment of alloys until the discovery of duraluminum and its heat treatment by Wilm.⁽⁶⁴⁾ Merica's explanation of the role of CuAl_2 in the hardening of copper-aluminum alloys, followed by Jeffries and Archer's use of these alloys to illustrate their slip interference theory of hardening, caused a wide interest in heat treatment of alloys in general. The role of Mg_2Si in the age hardening of duraluminum and of Rosen-

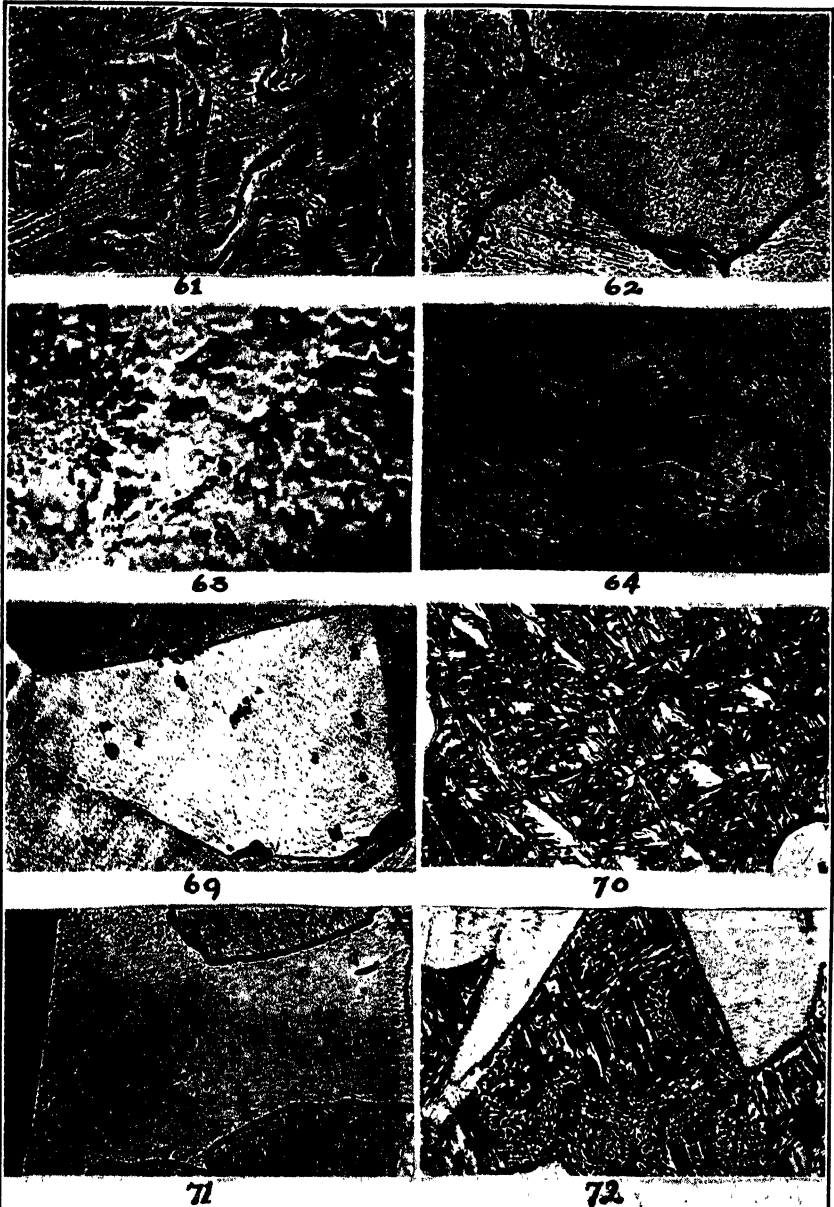


FIG. 61.—GUN METAL; INHOMOGENEOUS ALPHA AND EUTECTOID. $\times 450$.

FIG. 62.—SAME; OXIDE FILMS. $\times 450$.

FIG. 63.—TIN OXIDE IN BRONZE. $\times 90$.

FIG. 64.—SAME. $\times 400$.

FIG. 69.—MANGANESE BRONZE, QUENCHED FROM 740°C ; BETA. $\times 500$.

FIG. 70.—SAME, QUENCHED FROM 710°C ., DRAWN TO 300°C ., MARTENSITIC. $\times 500$.

FIG. 71.—NAVAL BRASS, QUENCHED FROM 600°C ., ALPHA AND BETA. $\times 500$.

FIG. 72.—SAME; QUENCHED FROM 600°C ., DRAWN TO 400°C ., ALPHA AND EUTECTOID. $\times 500$.

(REDUCED ONE-THIRD.)

hain's Y alloy was brought out by the Eleventh Report of the Alloys Research Committee.⁽⁶⁵⁾

Recently Dean, Zickrick and Nix⁽⁶⁶⁾ have shown that lead can be hardened by antimony in exactly the same way, and now there is a renewed interest in solubility curves in solid metals. Probably the most remarkable results are those obtained by Sykes⁽⁶⁷⁾ in the hardening of iron by molybdenum on quenching and ageing.

In all of these cases the results depend on heating the alloy to a temperature above the solubility curve in order to obtain a homogeneous solid solution, followed by a quench. The alloy is then aged to allow the precipitation of the phase in solution in what is called "critical dispersion" to obtain the best physical properties.

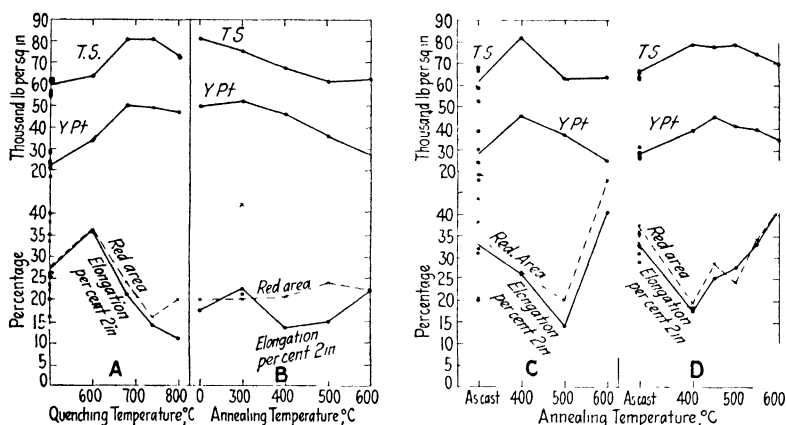


FIG. 65.—EFFECT OF QUENCHING AND TEMPERING ON MANGANESE BRONZE: A, CZX.216 (Cu 59.33, Zn 38.0, Fe 0.98, Mn 0.76, Sn 0.62, Al 0.22, Pb 0.13) HELD 1 HR. AND QUENCHED; B, SAME ALLOY QUENCHED AT 710° C., REHEATED FOR 1 HR. AND SLOWLY COOLED; C, CZX.215 (Cu 59.6, Zn 32.7, Fe 1.31, Mn 0.56, Sn 0.45, Al 0.10, Pb 0.17) HELD FOR 1 HR. AT 725° C. AND QUENCHED, REHEATED FOR 1 HR. AND SLOWLY COOLED; D, CZX.217 (Cu 58.75, Zn 30.9, Fe 1.25, Mn 0.83, Sn 0.47, Al 0.09, Pb 0.17) HELD FOR 1 HR. AT 725° C. AND QUENCHED, REHEATED FOR 1 HR. AND SLOWLY COOLED.

Simpler forms of heat treatment are found in the case of castings such as gun metal, the aim being to make the cored inhomogeneous alpha grains and dendrites homogeneous by diffusion and absorb the small patches of eutectoid. Work along this line has been done by Rawdon,⁽⁶⁸⁾ by Smart⁽⁶⁹⁾ and by Comstock.⁽⁷⁰⁾

Rawdon found that although the tensile strength of gun-metal castings was not materially affected, there was a great increase in ductility when annealed between 600 and 700° C. Smart records an appreciable increase in tensile and a very marked increase in elongation in bars annealed at 600° C., and Carson⁽⁷¹⁾ found a slight maximum in tensile strength on annealing at 700° C. for one hour, but the elongation was doubled by annealing at 650 to 700° C.

Very little has been published on the heat treatment of manganese bronze. Comstock says that the effect of quenching manganese bronze in water from a red heat is to fill the metal with invisible cracks and ruin the tensile properties.

At Columbia, however, various samples of manganese bronze have been quenched and tempered with marked increase in tensile strength and yield point, though at some sacrifice in ductility. Young⁽⁷²⁾ showed an increase in strength from 60,000 lb. per square inch as cast to 80,000 lb. when quenched from 700° C. Tempering causes a gradual decrease in strength as shown in the accompanying chart, Fig. 65. Two other series are also shown, which unfortunately do not give the physical properties as quenched.

Similar experiments were made with Naval brass by Carson.⁽⁷¹⁾ The metal as cast had a tensile strength of a little over 34,000 lb. per square

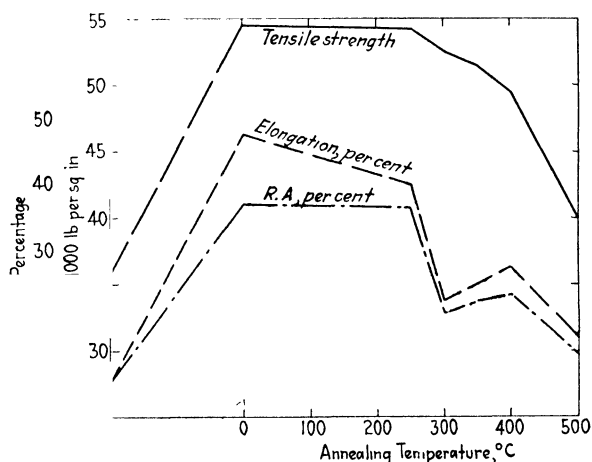


FIG. 66.—EFFECT OF HEAT TREATMENT OF NAVAL BRASS DRY-SAND CASTINGS (LAB. SER. CZX.349, Cu 62.85, Zn 35.27, Sn 1.84, Fe 0.04, Pb 0.00).

inch and an elongation of about 8 per cent. Quenching from 600° C. gives a tensile strength of 54,000 lb. per square inch and an elongation of 44 per cent. Tempering has little effect up to 250° C. but beyond this both the strength and ductility fall off, as shown in Fig. 66.

The changes of structure in both manganese bronze and Naval brass due to heat treatment are very interesting, and explain the changes in the physical properties.

Cast manganese bronze consists of small rods and granules of alpha in a matrix of golden yellow beta. It resembles Muntz metal. On heating, the beta tends to dissolve the alpha until the solubility curve passed and we have nothing but beta (see Fig. 59). By quenching this beta can be retained. Fig. 69 shows a sample quenched at 740° C., $\times 500$, and consists of beta grains with a few spicules of the blue constituent

characteristic of most manganese bronzes. Now in tempering, the beta tends to break down and precipitate the excess alpha and a beautiful martensitic structure results. Fig. 70 shows a sample, $\times 500$, quenched at 710°C. and tempered at 300°C. producing a structure near akin to martensite.

Cast Naval on the other hand consists of alpha grains with a network of eutectoid. When quenched from above the eutectoid change the metal consists of alpha and beta. Fig. 71 shows the effect of quenching at 600°C. , which gives alpha and beta, $\times 500$. On tempering the beta tends to break down into the eutectoid again, but as the hard gamma usually precipitates in the crystallographic planes of the beta, a martensitic effect often results, as Fig. 72, $\times 500$, shows where the sample was quenched at 600°C. and drawn at 400°C. , producing alpha and eutectoid.

A Short Summary in the Heat Treatment of Commercial Brasses and Bronze Castings

Gun Metal.—Copper 88, tin 10, zinc 2. The results of annealing depend to a great extent on the original composition and structure. Heating to 700°C. for 1 hr. produces homogeneous alpha and dissolves all of the eutectoid. In the case of good castings, this may give a decided increase in strength, and a marked increase in ductility. Most castings, however, are not good and show numerous cavities and films. If annealing causes the surfaces of these films to oxidize, slight improvement occurs, in fact the annealed material is generally poorer than the cast because the improvement caused by the more homogeneous structure is more than balanced by the deterioration due to the enlargement of the films. Where castings show high strength but are low in ductility due to segregation of the eutectoid, it will be found advantageous to anneal at from 600 to 700°C.

Bearing Bronze.—Copper 84, tin 12.5, zinc 3.5. The effect of annealing on microstructure is of the same nature as that in gun metal. The alpha grains become homogeneous and the eutectoid is taken into solution up to the saturation point of the alpha which is over 12 per cent. Sn. Annealing, therefore, results in a slight increase in tensile strength, a drop in yield point and a marked increase in the ductility. Annealing between 600°C. and 700°C. may be resorted to where improvement in tensile strength and ductility are required. In the case of the lead-bearing metal, there is a tendency for the lead to oxidize at the surface when the higher temperature is used.

Phosphor Bronze.—As in gun metal, the effect of annealing depends on the original structure. Annealing tends to make the alpha homogeneous and causes the eutectoid to go into solution. In faulty material, due to films, annealing may make the metal worse due to oxidation of the film surfaces. The general effect of annealing on the strength and ductility is the same as in gun metal. In this work 600°C. caused marked increase in the elongation without affecting the strength.

Cast Bronze.—Copper 63, zinc 32, tin 2, lead 3. On account of the fact that there is more than enough eutectoid to saturate the alpha grains with tin on annealing, but slight improvement can be expected as in the case of H metal. To get any marked improvement, the metal ought to be quenched from about 600°C. as in the case of Naval brass.

Naval Brass.—Copper 63, zinc 35, tin 2. As in the last material, there is more eutectoid than can be dissolved by the alpha hence annealing has no very marked

effect on the strength or ductility. On the other hand by quenching at 600° C. an enormous increase in tensile strength and ductility results. The metal ought not to be drawn above 250° C. otherwise loss in ductility occurs. This is due to the fact that quenching produces a mixture of alpha and beta, resembling Muntz metal. Annealing at 300° C. or higher causes the unstable beta to break down, due to the precipitation of the hard gamma constituent with a resulting loss of ductility.

Manganese Bronze.—The effect of annealing on manganese bronze depends on the original structure. Metal which has been very rapidly cooled may have its ductility increased by annealing to 600° C. followed by slow cooling. The effect of quenching and tempering varies with different grades of material. Sometimes a very marked increase in strength and a more marked increase in yield point can be obtained by quenching at temperatures between 600 and 650° C. without reducing the ductility below specifications. The effect of drawing this material after quenching, is to decrease the strength progressively with perhaps a slight decrease in ductility. An anneal at 300° C. is sufficient to remove quenching strains. In other cases, the effect of quenching, while it increases the tensile strength and yield point, is to ruin the elongation and this can not be restored even by reheating to high temperatures. It would therefore seem that no rules can be formulated in regard to manganese bronze as regards its behavior on quenching and tempering and that each different grade must be tried out by itself.

THE APPLICATION OF METALLOGRAPHY TO NON-METALLIC MATERIAL

The success of the use of metallographic methods applied to the commoner alloys led to investigations outside the field of metals.⁷ Thus the phosphides, silicides, sulfides, selenides, tellurides, arsenides, the mattes and speisses have been investigated notably by Friedrich⁽⁷³⁾ and his associates. At the same time the silicates systems have been most carefully and thoroughly studied. In this connection the work of the Geophysical Laboratory is of outstanding importance and the ternary systems of $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-MgO}$ have been accurately determined. McCaffery⁽⁷⁴⁾ has worked out the quaternary system and is now applying it to iron blast-furnace slags. Unfortunately, we yet lack knowledge of the systems containing FeO , and until we do have this, open-hearth slags will remain an unsolved problem as far as constitution.

Professor Howe was always hoping that someone would devote himself to the study of the constitution of slags. He frequently emphasized the absurdity of giving formulae to what are undoubtedly mechanical mixtures, and said that it was only want of courage that made us afraid to cast off the old ideas of formula, which was inexcusable in view of Vogt's work of 1903.⁽⁷⁵⁾ And here one might recall the discussion of the two famous metallurgists, as to the constitution of speiss in lead blast-furnace smelting, was it Fe_5As or Fe_5As_2 ? Under the microscope of course both are mechanical mixtures, being alloys of Fe and Fe_2As , which form a eutectic of 30 per cent. As at 840° C.

⁷ A summary of the non-metallic systems is given in Liddell's Handbook of Non-Ferrous Metallurgy. (1926), 1, 45.

A considerable amount of work has been done on the salts and this has been used in metallurgy, especially as applied to baths, fluxes and the like.

One of the most interesting studies is that of opaque ores.⁽⁷⁶⁾ We have manuals by Murdock,⁽⁷⁷⁾ Davy and Farnham,⁽⁷⁸⁾ Schneiderholm⁽⁷⁹⁾ and by Van de Veen,⁽⁸⁰⁾ setting forth the methods and application. The wonderful work of Graton and Murdoch,⁽⁸¹⁾ of Tolman and Rogers⁽⁸²⁾ show what can be accomplished. Here again Professor Howe showed a keen interest and some of the early work was done in his laboratory on the nickeliferous pyrrhotites,⁽⁸³⁾ on the titaniferous magnetities and other material⁽⁸⁴⁾ at the instigation of Professor Kemp.

Probably the newest application is the examination of polished sections as an aid to problems in ore dressing. The minute associations of the opaque constituents can only be determined in this way and the method has been made part of the laboratory work in Professor Taggart's course at Columbia.

WIDESPREAD INFLUENCE OF PROFESSOR HOWE

How much credit in the development of the new science of physical metallurgy is due Professor Howe is not generally understood. His influence was not limited to his own students as a letter from Dr. Jeffries so amply testifies.

I received my first metallographic training at the South Dakota State School of Mines, from Professor Fulton, who was one of Howe's students and admirers. He used Howe's "Iron, Steel and Other Alloys" as a text, and I strongly suspect that it was the clarity with which Howe presented his subject, together with the very clear method of putting Howe's results before us by Professor Fulton that gave me a leaning towards metallography. "Iron, Steel and Other Alloys," at the time I was in school, proved to be the most stimulating of any of the books to which I had access. In addition I was always eager to read Professor Howe's technical papers.

At Case School of Applied Science prior to 1914, I had done considerable work on grain growth in metals, but in 1914 I became especially interested in the subject because I was studying drawn tungsten wire which was used for lamp filaments, and the subject of grain growth is one which is vital in that connection. In this study I arrived at what seemed to me to be some new principles of grain growth and, because I considered Professor Howe the world's authority on this subject, I arranged to visit him at his home at Bedford Hills to discuss these principles with him. This was on July 1, 1915. Professor Howe was much interested in my results, and we began a correspondence which only ended with his untimely death.

While I was preparing to present my findings in the form of a paper, Mathewson and Phillips, work on "Recrystallization of Cold-Worked Alpha Brass on Annealing" was published. I presented in a discussion of this paper the elements of what is now known as the germinative temperature hypothesis of grain growth, which I first called critical temperature for grain growth. I then began preparation of a more extensive paper which was later published under the title "Grain Growth Phenomena in Metals." At the same time Professor Howe began preparation of his paper "On Grain Growth" and used my discussion of the paper by Mathewson and Phillips as

the basis for his paper. We corresponded freely with each other during the preparation of both of these papers, and it was by private correspondence that he informed me of this suggestion to use "germinative temperature" in place of "critical temperature" for grain growth. He insisted that my paper on grain growth phenomena in metals be published ahead of his because, as he put it in a letter to me: "I do not wish it to appear that I am stealing your thunder."

The correspondence with Howe was most pleasant. It was indeed fortunate that he was able to give his attention to this subject of grain growth because he had the faculty of presenting things so clearly in writing that the subject matter became more generally understood and adopted. The science of metallography was therefore greatly enriched because he took up anew his subject of grain growth in 1916 and later.

With reference to the general theory of hardness which I believe was crystallized by Archer and myself, one of the principles of slip interference is the "obstruction principle." This principle was named by Howe and the mechanism was clearly explained by him. It is that portion of the slip interference theory which deals with the obstruction of slip in a soft constituent by the presence of a harder substance, the harder substance being present in particles of the same order of size as the grains of softer metals themselves. Unfortunately Howe did not carry his principle to its more or less logical conclusion, namely, to the slip interference caused by very small particles imbedded within a larger crystal. Had he done this it is very likely that he would have put forward the theory about as it now stands, well in advance of his death. His contribution to the subject of hardness and hardening, however, can hardly be overestimated because he made it possible for hundreds of workers in this field to gain a clearer conception of the internal structure of metals and the relation between structure and properties to which our present theories represent only extensions. Of all of the workers of the world in the field of metal science, it seems to me that Howe's influence has been the greatest.

Perhaps I have wandered a little afield, from my purpose to show martensitic structures in alloys resulting from quenching or quenching and tempering, just as in steel. If I have seemed to dwell too much on the work done at Columbia, it was because I wanted to give examples which came from Howe's laboratories—for he it was who laid the foundations and began our work of research, in physical metallurgy, who suggested and generally guided all of the work that was done during his professorship, and when he became emeritus professor he continued to inspire us with his visits and suggestions. Nay, more, he so drilled us all in his methods, and clear manner of thinking that today we can say with some little truth his way is our way and I trust always will be.

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INDEX

NOTE: In this index the names of authors of papers and discussions and of men referred to are in SMALL CAPITALS, and the titles of papers in *italics*. Roman numeral pages refer to mention of papers.

- Abrasive sands photomicrographs, 441-444.
properties and uses, 439-443.
- Action of Reducing Gases on Heated Copper* (BASSETT and BRADLEY), xxvi, 755, Discussion, 770-775.
- Admiralty tube, structure, photomicrograph, 1140.
- Adsorbent films: see *Film water*.
- Adsorption theory, modification, aluminum-silicon alloys, 585.
- Aerator tank, construction, 95.
- Aerators: see *Ferric sulfate and sulfuric acid, from roaster gas*.
- Age-hardening, alloys, method, discussion, 539
- Air: density, variability, 1011.
oxygen content: 1011.
weight, 1011.
see also *Open-hearth furnace*.
- Air gap: see *Neumann bands, formation*.
- Air lifts, Standard Reduction Co. null, 336.
- Air Sand Process of Cleaning Coal* (FRASER and YANCY), xxvii.
- Air Service (U. S.) specifications, casting Al-Cu-Si specimens, 466.
- Ajo, Ariz.: see *New Cornelia Copper Co.*
- Alabama, stone-sawing sand, photomicrograph, 442.
- Alaska (Petroleum Production)* (SMITH), xxiv.
- Albany sands: comparison with furnace-bottom sand, 390.
stripping: problems, 381-382.
view, 383.
- ALEXANDER, H. H.: *Discussion on The Conductivity of Electrolytes Used in the Electrolytical Separation of Gold and Silver*, 121.
- Alkalies, in glass sands, occurrence and effect, 405.
- Alkali-halide crystals: see *Atomic structure*.
- Alkaline concentrations, flotation, sulfides, effect, 356, 361.
- ALLEN, H. P.: *Discussion on Chloridizing Mill of the Standard Reduction Co.*, 338.
- ALLEN, H. P. and MADGE, W. C.: *Chloridizing Mill of the Standard Reduction Co.*, xix, 317-338.
Tintic Standard Co.'s Mill, xviii.
- ALLISON, V. C.: *Explosibility of Coal and Other Dusts in a Laboratory Steel Dust-gallery*, xxvii.
- Allotropic theory, steel hardening, 1145.
- Allotropy, definition, discussion, 856.
- Alloys: constitution, discussion, 1161.
heat treatment: effect: 1168.
curves, 1170, 1171.
see also *Non-ferrous alloys* and alloys, named.
- Alpha iron: arrangement of atoms, diagrams, 852
characteristic Neumann bands, 966.
solubility of carbon in, 1146.
theory, steel hardening, 1145.
- Alumina: in electrolyte, effect, 61, 80.
in glass sands, occurrence and effect, 401.
- Aluminum: effect in brasses: 805, 816, 825.
photomicrographs, 808, 827, 828.
impurities in, effect on solubility of copper, 579.
in open-hearth slag: variation, 1083, 1090.
during working period, curve, 1090.
- Aluminum alloys: intercrystalline brittleness, photomicrograph, 753.
slow cooling: effect: 575.
photomicrographs, 575-576.
structure photomicrographs, 3158.
see also alloys named.
- Aluminum brass: effect of iron, data, 824.
effect of nickel: 816-822.
data, 803, 823.
photomicrographs, 804, 805.
effect of nickel and iron, data, 826.
effect of nickel and tin: data, 826.
photomicrographs, 827, 828.
introduction of nickel and iron, method, 826.
introduction of nickel, method, 816.
- Aluminum bronze: diagram, sketch, 1157.
iron in, effect, data, 1159, 1160.
manganese in, effect, data, 1160.
nickel in, effect, data, 1160.
- Aluminum-copper alloys: aluminum end, diagram, 567.
cooling curves, tests, description, 562.
equilibrium relations: discussion, 568-574.
tests and results, 560-580.
eutectic temperature, 568.
hardness, data, 476-478.
discussion, 469.
photomicrographs: different amounts of copper, 565-566.
melted areas, 569, 570.
precipitation theory, 577.
slip interference theory, 578.

- Aluminum-copper alloys: specific gravity, 469, 476-478.
test specimens: description, 561, 580.
preparation, 561.
- Aluminum-copper-nickel-manganese alloys: see *Piston alloys*.
- Aluminum-copper-silicon alloy: casting, specifications, 466.
gated, views, 465, 466.
heat treatment: factors controlling, 464.
specifications, 466.
mechanical property tests: 467-469.
results: curves, 470-472.
data, sand cast, 476.
heat-treated, 477-478
discussion, 471.
shear tests: 467.
data, 476-478.
structures, photomicrographs, 473-475.
uses, 465.
"X constituents," composition, 625, 626.
effect, 622.
- Aluminum-iron-silicon alloys: equilibrium. determination, 622-626.
diagrams, 624, 625.
silicon in, function, 464.
- Aluminum-silicon alloys: advantageous properties, 616.
constitution: 582.
diagram, 586.
discussion, 586, 621.
iron in, limits, 619.
occurrence, manner, 582, 583, 587.
largest cast, 620.
modification: effect, 582.
experiments: conclusions, 616.
method, description, 591.
raw materials, chemical analyses, 591.
results: curves, 595, 597, 598, 600.
data, 596, 599-602.
discussion, 613.
summary, 618.
process, 587.
theories, 585.
modified: annealing, effect, 621.
effect of iron, 598.
photomicrographs, 583, 584, 603-613
physical properties: effect of iron, 602, 615.
effect of silicon, 601.
sodium loss on standing: curve, 594.
data, 596.
discussion, 590.
test bars, chemical analysis, 594.
Navy specifications, 619.
normal: photomicrograph, 582, 583.
physical properties, 600.
normal and modified, properties, curves, 597.
sand cast, modification, definition, 581.
silicon content, effect, curve, 600.
test bars: chemical analyses, 599.
molds, views, 590, 593.
- Alundum hood, determination of fusion temperatures, view, 969.
- American Brass Co., determining sulfur and oxygen in refined copper, apparatus, view, 785.
- American Foundrymen's Assoc., joint meeting, xx.
- American Glass Sands, Their Properties and Preparation* (FETTER), xxv, 398; Discussion, 422-423.
- A. I. E. E., joint session, xxii.
- A. I. M. E.: Directors, 1926, 1927, xi.
meetings: Casper, Wyo., sessions, xix
New York, 1926, xxi.
sessions, xxii.
Salt Lake City, 1925, xvii
sessions, xviii.
Syracuse, xx.
sessions, xx.
members, deaths, notices, xxxi, xxxii
officers, 1926-1927, xi.
publications, policy, iii
Salt Creek field, symposium, xix
- American Smelting & Refining Co.: A. I. M. E. trip, xvii.
Murray, Utah, plant, equipment, 173.
- A. S. C. E., joint session, xxii.
- A. S. M. E., joint session, xxii.
- Ammonia, blowholes in rimmed steel, discussion, 1032, 1036, 1042, 1045
- Ammoniacal peroxide, as etching reagent, 733
- Ammonium nitrate: see *Electrolytes, gold and silver separation*.
- Amorphous Cement and the Formation of Ferrite in the Light of X-ray Evidence* (FOLEY), xx, 850, Discussion, 857-858
- Amorphous intercrystalline cement, criticism of theory, 855
- Amorphous-iron theory, steel hardening, 1145
- Anaconda Electrolytic White Lead* (BOWMAN), xxv, 146.
- Anaconda leaching plant, data, 106.
- Anaconda Lead Products Co.: see *Sperry process, electrolytic white lead*.
- Analyses: see *Copper, conductivity and ductility test; Copper tubes; Ferromanganese; Ferrosilicon; Heterogeneous rocks; Homogenous rocks; Illuminating gas; Industrial sands; Lead blast-furnace, slag; Nickel silver, test specimens; Open-hearth process, equilibrium tests, Slag, steel bath during run; Tube-mill feed and products*.
- ANDERSON, A. E.: Discussion on. *Recovery of Copper by Leaching, Ohio Brass Co of Utah*, 56, 57.
- ANDERSON, A. E. and CAMERON, F. K.: *Recovery of Copper by Leaching, Ohio Copper Co of Utah*, xviii, 31.
- Annealing: duration, copper-aluminum alloys, effect, 572.
see also *Aluminum-silicon alloys; Iron, cold-worked ingots; Lead-antimony alloys*.
- Annealing cracking: see *Nickel silver*.
- Annealing Cracking of the Nickel Silvers* (JONES and WHITEHEAD), xx, 834; Discussion, 849.
- Annealing of Commercial Copper to Prevent Embrittlement by Reducing Gases* (LEITER), xxvi, 776; Discussion, 782-783.

- Anode slime, Sperry process, production and recovery, 166.
- Anodes: efficiency, variation, control, 61.
graphite, characteristics, 60.
leaching copper ores, choice, 60
lead, characteristics, 61
molding and pressing, electrolytic white lead, 150-152.
precious metal content, ratio to percentage loss, 144.
stripping, Nichols series process, 137
see also *Electrolysis, copper, Nichols series process; X-ray anode*
- Anodic oxidation. ferrie iron by, cheapness, 98
use and advantages, leaching and reduction, 85.
- Antiacid, as a term in copper leaching, 81
- Anti-knock Gasolines and Special Engine Development* (SPARROW), xxiii.
- Antimony, solubility in lead 507.
effect of aging, curve, 510.
- Antimony-lead alloys see *Lead-antimony alloys*
- Antimony-tin-lead alloys: see *Lead-antimony-tin alloys*.
- Apochromatic system, comparison with monochromatic, 919
- Appalachian Fields (Petroleum Production)* (TURNBULL), xxiv.
- Application of Cottrell Process in Lead and Copper Smelting* (LABBE), xviii.
- Application of Mining Tax Laws to the Petroleum Industry* (DANFORD), xix.
- ARCHER, R. S.: *Discussions on The Lead Antimony System of Hardening of Lead Alloys*, 539
Modification and Properties of Sand-cast Aluminum-silicon Alloys, 620-621.
- ARCHER, R. S. and KEMP, L. W.: *Modification and Properties of Sand-cast Aluminum-silicon Alloys*, xxv, 581-619
- Arcofrax, physical properties, 392
- Arcents' siphon tap, removing lead from blast furnaces, 187.
- Argentine (Petroleum Production)* (OSTRANDER), xxiv
- Arizona: see *Nogales*.
- Arkansas and Louisiana (Petroleum Production)* (RING), xxiv.
- Arnico iron, test for Neumann bands, 965
- Armor structure: description, 1154.
photomicrographs, 1152, 1153.
- ARMSTRONG, R. O. and RADER, C. M.: *Water Shut-off Methods in Salt Creek Field*, xix.
- ARNOLD, J. O., on hardening of steel, 864, 865, 869, 870, 884, 1145
- Arsenic: effect on conductivity of copper, 693, 694.
removal from silver precipitate, 321.
- Arsenic fume, lead smelting, treatment and recovery, 195.
- Arsenic kitchens, description, 196.
- Arsenical copper: see *Copper*
- Ash, in coke, variation, 1016.
- Assay; see *Standard Reduction Co. ore*.
- Atomic structure, alkali-halides: compressibilities, 646.
crystals. data, 644.
diagram, 643.
discussion, 642
lattice energies, 646.
pressure coefficients, 646.
bibliography, 653.
crystal formation: controlling forces, 641.
diagrams, 637, 641, 642, 648
description, 628.
diagrams: 637, 641, 642, 648
electrons: arrangement and behavior, discussion, 633-639
arrangement by elements, 631-633.
orbits, NaBr crystal, sketch, 644.
magneton numbers, rare earths, 639, 640
metals: ion-electron lattice, 648, 650.
lattice structure, 647.
phenomena, discussion, 651
quantum theory, characteristics, 630.
research needed, 628, 653
typical spectra, view, 635
- Austenite: composition, discussion, 851.
constitution, 1147.
hardening of steel: effect, 860
temperature, 1146
transformation: effect, 1146.
to pearlite: diagrams, 880
discussion, 881.
ultra-violet light: selective characteristics: 924.
photomicrographs, 919-921.
- Australasia (Petroleum Production)* (CLAPP), xxiv

B

- Baghouse. lead smelter. description, 192, 194-196.
first use, 173.
volatilization null, 208
- BAIN, E. C.: on hardening of steel, 864, 865, 869, 870, 884.
- BAKER, J. A.: *Discussions on: Classification in Witwatersrand Mills*, 251
An Investigation of Crushing Phenomena, 313, 314
Mechanism of Filtration, 234.
- BALL, M. W.: *Naval Oil Reserves*, xix.
- Ball indentation test: see *Meyer's analysis*.
- Ball milling, advantages compared with stamps, 312
crushing action, 311-312.
- Ball mills, -200-mesh material, computed and observed, data, 288.
particle breakage, manner, 286.
size of balls, effect, 284.
- Ball test, versus conical point test, discussion, 674, 675.
- Balls, relation to size of particle and nip angle, 277
- Baltimore Copper Smelting & Refining Co.: electrolytic method, characteristics, 123.
- BARDWELL, CARLOS, SACKETT, B. L., JACOBSON, SIMON, JENSEN, N. H., and: *Lead Smelting in Utah*, xviii, 171-197.

- BARDWELL, E. S. and MILLER R. S.: *Use of Pulverized Coal in Copper Refining Furnaces*, xviii.
- Barium crystal, ion-electron lattice, 649.
- BARKEE, L. M. and MIX, B. E.: *Method of Unloading and Coarse-crushing Practice at Magna Plant of Utah Copper Co.*, 212-223.
- BARTRAM, J. G.: *Sketch of Geology and Formations of Central Wyoming*, xix.
- BARTRAM, J. G. and WILSON, J. H.: *Core Drilling in Geologic Exploration as Applied in Wyoming and Montana*, xix.
- Basic Changes in Refining Processes* (MILLER), xxiii.
- Basic process: see *Open hearth process*.
- Basicity index, open-hearth slag, 1111.
- Bas-relief: see *Metallography*, ultra-violet.
- BASSETT, W. H.: *Discussion on: Hardness of Copper and Meyer's Analysis*, 676.
- BASSETT, W. H. and BEDWORTH, H. A.: *Estimation of Oxygen and Sulfur in Refined Copper*, xxvi, 784-797; *Discussion*, 797-799.
- BASSETT, W. H. and BRADLEY, J. C.: *Action of Reducing Gases on Heated Copper*, xxvi, 755-770.
- Ezudations on Copper Castings*, xxvi, 700-705.
- Batch ball-mill: see *Homogenous rocks*.
- Batch rod-mill: see *Homogenous rocks, rod-mill products*.
- Batch scum, glass sands, formation, 407.
- BATES, B. R.: *Classification in Witwatersrand Mills*, xxv, 239-249.
- Discussions on: Classification in Witwatersrand Mills*, 249-252.
- Mechanism of Filtration*, 238.
- Bath: see *Open-hearth process*.
- Bear Mountain Bridge, N. Y., A. I. M. E. trip, xxii.
- BEARD, A. A. and BONNEL, R. A.: *Cleaning Oil Wells by Compressed Air*, xix.
- Bearing bronze, heat treatment, 1172.
- BEDWORTH, H. A.: *Discussion on: Estimation of Oxygen and Sulfur in Refined Copper*, xxvi, 798.
- BEDWORTH, H. A., and BASSETT, W. H.: *Estimation of Oxygen and Sulfur in Refined Copper*, xxvi, 784-797.
- BEESON, J. J.: *Ore Deposits and Their Relation to Structural Geology*, xviii.
- Beet sugar, filtration, practice, 236, 237.
- BELAJEW, N. on harding of steel, 865, 868, 870, 884.
- Belle Forché, S. Dak., bentonite, physical properties, 392.
- Belt conveyors: see *Magna plant*.
- BENEDICKS, C., on harding of steel, 863, 865, 868, 870, 886.
- BENGOUGH, G. D. and HILL, B. P., on the effect of reducing gases on copper, 744.
- Bentonite: as bond, disadvantages, 391.
- Belle Forché, S. Dak., physical properties, 392.
- composition variation, 393.
- market prices, 389.
- possible use, 388-393.
- Berkeley Springs, W. Va.: glass sands: grades, 419.
- occurrence, 415.
- BERKEY, C. P., photomicrographs by, count of grains and grain size, 304-306.
- Bibliography: atomic structure, 655.
- metallography, 1175.
- BILLINGS, T. P.: *Discussion on Recovery of Copper by Leaching, Ohio Brass Co. of Utah*, 57.
- Billy Creek Field (GEIS), xix.
- Bingham Canyon, Utah: see *Ohio Copper Co. mine*.
- Bingham district, Utah, ores, description, 312.
- BINGHAM, E. C., on seepage, 226.
- Bingham mines, leaching water from, disadvantages, 44.
- Bingham, Utah: water jacket used in lead smelting, 171.
- see also *Ohio Copper Co. of Utah*.
- Biographies, deceased members, xxix.
- BIRD, R. M.: *Mining and Preparation of Eastern Molding Sands*, xxv, 381-388.
- Discussion on Mining and Preparation of Eastern Molding Sands*, 388, 390, 391.
- Blast furnace: calculations, probable error, 1009.
- charge: constituents, variability, 1009.
- weight, possible error in, 1009.
- oxygen consumption per pound of coke, 1015, 1024.
- see also *Lead blast-furnaces*.
- Blast-furnace committee, xiii.
- Blast Furnace Plant of the Columbia Steel Corporation* (JACKSON), xviii.
- Blast-furnace slag: see *Ferrous slags*.
- Bhster: see *Copper*.
- Blower, gas, description, 91.
- Blowholes: see *Rimmed steel*.
- Blowing, copper matte, in converters, discussion, 195, 197-198.
- BLUM, W.: *Discussion on: The Conductivity of Electrolytes Used in the Electrolytic Separation of Gold and Silver*, 117.
- Boiler rivet, structure, photomicrographs, 1149.
- Boiler tube, structure, photomicrographs, 1145, 1152.
- Bolco, Calif., shallow electrolyte tank at, 143.
- Bonds: physical properties, tests, 392.
- see also *Carborundum, mounting, Seger cones*.
- BONNEL, R. A. and BEARD A. A.: *Cleaning Oil Wells by Compressed Air*, xix.
- BOOTH, LIONEL: *Development of Differential Flotation on Complex Ores*, xviii.
- Borate deposits: control of, 435.
- origin, determination, importance, 461.
- stratigraphy, 460.
- see also *Colemanite; Kramer, Calif; Searles Lake; Ulexite*.
- Borate Deposits near Kramer, Calif.* (GALE), xxv, 449-463.
- Borax Consolidated Ltd., control of borax land, 453.
- Borax mining claims, disputes, 461.
- Bornite, solubility, 75.
- Bowl classifiers, as concentrator, use, 249.
- see also *Dorr bowl classifiers*.

- BOWMAN, R. G.: *Anaconda Electrolytic White Lead*, xix, 146-170.
- BOYLSTON, H. M., on hardening of Steel, 863, 865, 886.
- BRADLEY, J. C. and BASSETT, W. H.: *Action of Reducing Gases on Heated Copper*, xxvi, 755-770.
- Exudations on Copper Castings*, xxvi, 700-705.
- BRASS, aluminum in, effect: data, 806.
photomicrographs, 808.
see also *Aluminum brass*.
casting, procedure, 831.
constitutional diagrams, development, 1166.
failure, causes, 1167.
heat treatments, summary, 1172.
impurities, effect, 828.
iron in, effect, data, 812.
photomicrographs, 813-815.
introduction, 811.
melting, difficulties, 830.
rules, 829.
scrap, discussion, 831.
molding, materials, discussion, 832.
procedure, discussion, 831.
nickel in, effect, 802.
normalized condition, definition, 799.
special, analyses, 800, 801.
standard, physical properties, 800.
tin in, effect, data, 809.
see also *Aluminum brass*; *Naval brass*; *Nickel brass*.
- BRAUN pulverizer, -200-mesh material, computed and observed, data, 288.
- BREAKAGE, rock particles: see *Heterogenous rocks*; *Homogenous rocks*.
- BREARLEY, H., on hardening of steel, 863, 865, 871, 886.
- BREWSTER, F. M.: *Spacing of Oil Wells*, xxiii.
- BRIDGETON, N. J., glass sands, photomicrograph, 411.
- BRIGHT, GRAHAM: *Data on Use of Loading Machines in Bituminous Mines*, xxvii.
- BRIGHTON, T. B., water-solubility tests, copper ore, 42.
Discussion on Recovery of Copper by Leaching, Ohio Copper Co. of Utah, 55.
- Brinell test, possible error, 657, 676.
- Briquetting: see *Ohio Copper Co., copper concentrate*.
- British Columbia: see *Premier mine*.
- Brittleness. see *Metals, intercrystalline brittleness*.
- BROKAW, A. D.: *Taxation and the Oil Industry*, xxii.
- Bronzes, analyses, 800.
failure, causes, 1167.
heat treatments, summary, 1172.
structure, photomicrographs, 1169.
see also *Aluminum bronze*; *Bearing bronze*; *Cast Bronze*; *Gun metal*; *Manganese bronze*; *Phosphor bronze*.
- BROOKS, B. T., DAY, R. B. and KNAPP, A.: *Economic Incidence of Cracking*, xxiii.
- BROWN, E. C.: *Core Drilling Technology. Basket Cores*, xxiii.
- Bubbler, rotating shear, types, 89.
- Bubbles; roaster gas making ferric sulfate and sulfuric acid; coalescence, remedy, 90.
size, 86, 89-90.
see also *Soap bubbles*.
- BUCK, V. B.: *Discussion on Making Rimmed Steel*, 1045.
- BULL, R. A.: *Discussion on Mining and Preparation of Eastern Molding Sands*, 389, 390, 391.
- Bureau of Mines: see *Ferric sulfate and sulfuric acid, from roaster gas*.
- Burma slags, high-zinc, content and behavior, 28.
- Busbars, Nichols series process, 132.
- Butte, Mont., district, low-grade zinc deposits, 6.

C

- Cadmium: crystal, ion-electron lattice, 649, 650.
lead smelting, recovery, method, 197.
- Cadmium spark, metallography, use, 916.
- ultra-violet photomicrographs, 917, 918, 923.
- Calcination: Utah lead ores. degree, 175.
method, 177.
- Calcium, open-hearth slag, variation, 1082, 1088.
- Calcium chloride, for roasting, source, 338.
- Calcium fluoride, crystal, atomic structure, sketch, 648.
- Calcium oxide: bonding property, development, 7.
open-hearth, slag, curve, 1088.
- Calcium sulfide, crystal, lattice structure, data, 644.
- Caldecott cones, for coarse product, 247.
- California: see *Boleo*; *Kramer*; *Searles Lake*.
- California (*Petroleum Production*) (GESTER and WAGT), xxiii.
- CALLEN, A. C.: *Discussion of Theory of Mine Ventilation*, xxiv.
- CALLOW, J. M.: *Discussion on Mechanism of Filtration*, 236, 237.
James Douglas medalist, 1926, xxii.
- CAMERON, F. K.: *Discussion on Recovery of Copper by Leaching, Ohio Brass Co of Utah*, 57.
- CAMERON, F. K. and ANDERSON, A. E.: *Recovery of Copper by Leaching, Ohio Copper Co of Utah*, xviii, 31.
- CAMPBELL, A. B.: *Discussion on Iron-tungsten System*, 1008.
- CAMPBELL, W., on hardening of steel, 864, 865, 868, 871, 887.
Last Twenty-five Years of Metallography, (Howe Memorial), xxvii, 1135, 1178.
- Car dumper, Magna plant, view, 217.
- Carbide: free, ultra-violet selective characteristics, 924.
in steel: heating, effect, 1146.
particle growth, cause, 1146.
precipitation: effect, 1146.
in all temperature effect, 1146.
- Carbide molecules, in martensite, position, 869.
- Carbon: in martensite, condition, 862.
open-hearth charge: decrease during run, curves, 1080, 1084.
effect, 1035, 1044-1045.

- Carbon: open-hearth equilibrium: laboratory data, 1123.
 plant data, 1124, 1125.
 temperature effect, curve, 1124.
 open-hearth process, elimination reactions, 1122.
 open-hearth slag, elimination curve, 1084.
 solubility, 1146.
- Carbon and iron, in martensite, bond, 865
- Carbon atoms: in martensite: position: 869.
 diagram, 896.
- Carbon dioxide: see *Copper drillings, ignition*.
- Carbon-free iron alloy, hardness, 1006.
- Carbon-iron: see *Iron-carbon*
- Carbon-iron system, equilibrium diagram, 853
- Carbon monoxide: blowholes in rimmed steel: effect, 1032, 1039.
 view, 1033.
- Carbon paper, use in focusing, 914.
- Carbon steel: air-cooled, photomicrograph, 934-936, 939, 941, 942.
 cooling tests: apparatus, 930.
 procedure, 930.
 results, 933.
 discussion, 932.
 specimens, preparation, 931.
 ferrite banded, photomicrograph, 945
 furnace-cooled, photomicrographs, 937, 938, 943, 944.
 impact values: effect of quenching temperature, 937.
 data, 940.
- Carbon theories, steel hardening, 1145.
- Carbonating system, Sperry process, 162
- Carborundum: mounting, Seger cones, bonds, 9
 use in furnace construction, 8.
- CARPENTER and EDWARDS, steel hardening theory, 1145.
- CARVER, R. D.: *Discussions on: Mining and Preparation of Eastern Molding Sands*, 390.
Standard Tests of Molding Sands, 397.
- Casper, Wyo., meeting, papers, xix
- Cast bronze, heat treatment, 1172.
- Casting, brass, procedure, 831.
 lead, 187.
- Casting machines and ladle, wire-bar practice, 140, 141.
- Cathode-charging chute, wire-bar furnace, 138.
- Cathodes: efficiency, variation, control, 61.
 impregnation with paraffin, 120.
 solubility in electrolyte, prevention, 72, 79.
 stripping, Nichols series process, 137.
 see also *Sperry process*.
- Cement: see *Amorphous intercrystalline cement*
- Cement copper: in discard solution, leaching, dissolving, 79.
 marketing, difficulties, 51.
- Cement-plaster sand, properties and uses, 445.
- Cementation, copper, versus electrolysis, 85, 98, 104-107.
- Cementite, in steel, precipitation, effect, 1146.
- Chalcanthite: appearance, mine and plant workings, 36.
 occurrence, Chile, 36.
- Chalcocite: Inspiration ore, accessibility to solution, 62.
 Ohio Copper Co. mine, 34.
 reaction to oxygen and water, equation, 34.
 reactions forming, 34.
 solubility, 75, 77.
- Chalcopyrite: recovery, 342.
 sodium-cyanide flotation tests, 370.
 solubility, 75, 77, 80.
- CHANCE, T. M.: *Mt Union Sand Flotation Plant for the Preparation of Bituminous Coal*, xxvii.
- CHARY and GRENET, steel hardening theory, 1145.
- Chase mill and screen, preparing glass sands, view, 414
- Chemical equilibrium: see *Open-hearth process, basic*.
- Chemical Equilibrium of Manganese, Carbon and Phosphorous in the Basic Open-hearth Process* (HERTY, JR.), xxvii, 1107, Discussion, 1133-1134
- Chemical sand, properties and uses, 445.
- Chemistry, iron and steel, committee, xii
- CHEVENARD, PIERRE on hardening of steel, 865, 868, 887
- Chief Consolidated coal-pulverizing plant: features, 208.
 flow sheet, 208.
 experimental plant: description, 202
 flow sheet, 203.
 gold, silver and lead recovery, 209
 mill: description, 206
 flow sheets, 205-208.
 mines, A I M E trip, xvii
 plant: coal consumption, 209
 crushing, flow sheet, 205
 equipment, views, 204.
 results, data, 209
 tonnage rate to kiln, 209
 process: concentration ratio, 210.
 oxidized tailings test, results, 203
 volatilization plant: flow sheet, 207
 view, 201.
 volatilization process: absence of salt in furnace feed, effect, 201.
 metals, form, 210.
 preliminary concentration, 201-202.
 wet concentrator, flow-sheet, 206.
- Chief Consolidated Volatilization Process and Mill* (WIGTON), xviii, 200; Discussion, 209-211.
- Chile, chalcantite, occurrence, 36.
- Chloride volatilization, early work, 209.
- Chloridizing mill, description and practice, 317-338.
- Chloridizing Mill of the Standard Reduction Co.* (ALLEN and MADGE), xix, 317; Discussion, 338-341.
- CHRISTIE, J. L.: *Discussion on Action of Reducing Gases on Heated Copper*, 771-772.
- CLAPP, F. G.: *Australasia (Petroleum Production*, xxiv.
- CLARK, L. F.: *Discussion on an Investigation of Crushing Phenomena*, 311.

- Classification:** clay balls, trouble with, prevention, 249.
feed: quality: importance, 244.
 data, 245.
 sand and gravel, 432.
sand-slime separation, cones versus bowls, 248.
speed, effect, 246.
tests, feed, quality, 245.
types, comparison, 239-244.
 see also *Witwatersrand mills*.
- Classification in Witwatersrand Mill (BATES),** xxv, 239; Discussion, 249-252.
- Classifiers:** heavy material in circuit, accumulation, 248, 250.
speed: effect, 244.
 tests, results, 247.
 see also *Cones; Dorr bowl; Dorr straight type*.
- Clay balls,** in classifiers, troubles, 249.
- CLAYDEN, A. L. and HORNING, H. L.:** *Economic Effect of Anti-knock Motor Fuels*, xxiii.
- CLAYTON, C. Y.:** *Effect of Annealing upon the Hardness of Cold-worked Ingot Iron*, xxvi, 926-928.
- CLAYTON, C. Y., REMMERS, W. E. and FOLEY, F. B.:** *Influence of Temperature, Time and Rate of Cooling on Physical Properties of Carbon Steel-II*, xxvi, 927-947.
- Cleaning Oil Wells by Compressed Air (BEARD and BONNEL),** xix.
- Cleaning Oil Wells by Heated Oil (KNOX),** xix.
- CLEVENGER, G. H.:** *Discussions on: Classification in Witwatersrand Mills*, 249, 250
Mechanism of Filtration, 235-238.
- Coal,** consumption, volatilization plant, 209.
- Coal and coke symposium,** papers, xxvii.
- Coalescence:** see *Copper*.
- Coal-pulverizing plant:** features, 208.
 flow sheet, 208.
- Coke:** ash in, variation, 1016.
 moisture, variability, 1016.
 relation to oxygen consumption, blast furnace, 1015, 1024.
- Coke and coal symposium,** papers, xxvii.
- Coke-oven gas,** open-hearth fuel, controlled combustion, data, 1068-1071, 1074, 1075.
- COLCORD, F. F., KERN, E. F. and MULLIGAN, J. J.:** *The Conductivity of Electrolytes in the Electrolytic Separation of Silver and Gold*, xxv, 108-117.
- Colemanite:** formation in place, 449.
 lode deposits, case for, 462.
 origin, theories, 452.
 see also *Kramer, Calif.*
- Colloid theory,** modification, aluminum-silicon alloys, 585.
- Colloidalty,** maximum, zone, discussion, 905.
- Colloids:** characteristics, 906, 907.
 intermediate zone of dispersion, 906.
- Colorado:** see *Leadville*.
- Columbia and Peru (Petroleum Production) (HUNTLEY),** xxiv.
- Columbia Steel Corp., A. I. M. E.,** trip, xvii.
- Combustion control:** see *Open-hearth furnace*.
- Combustion in the Open-hearth Furnace with Special Reference to Automatic Control (HUESENER),** xxvi, 1047-1078.
- Combustion products,** open-hearth furnace, weight, 1068.
- Combustion regulators,** sections, 1066, 1067.
- Committees, A. I. M. E.,** personnel, xii, xiii.
- Comparative Value as Motor Fuel of Cracked Gasoline vs. Straight Run Gasoline (WELLS),** xxiii.
- Compression tests:** AL-CU-SI alloy: 467.
 data, 476-478.
- Concentrates,** carrying and handling, 347.
- Concentration:** grinding, degree needed, 249.
 wet: see *Chief Consolidated plant; Lead*.
- Concentration papers,** list, xxv.
- Concentrator:** see *Gravity concentrator; Huff*.
- Condenser:** see *Arsenic kitchens*.
- Conductivities:** lead-antimony alloys: measurement: 508.
 curves, 509-512.
 see also *Copper; Electrolytes, gold and silver separation*.
- Conductivity of Electrolytes Used in the Electrolytic Separation of Silver and Gold (COLCORD, KERN and MULLIGAN),** xxv, 108; Discussion, 117-122.
- Cone classifiers:** comparison with straight and bowl classifiers, 239-243, 248.
 double, description and use, 345.
 tests: flow sheet, 240.
 results, 240.
- Conical-point test,** versus ball test, discussion, 674, 675.
- Consolidated Mercur Gold Mines Co.,** crushing costs, 340.
- Constitutional diagrams,** alloys, discussion, 1161.
- Contactors shunts,** flexible, copper wires, embrittlement, 749.
- Converter fume,** lead smelting, treatment, 195.
- Conveyors:** see *Magna plant*.
- Coolidge X-ray tubes,** anodes, leaks, causes, 748.
- Cooling:** see *Carbon steel*.
- Cooling cracks,** nickel silver, photomicrographs, 839, 841.
- Cooling curves,** Al-Cu alloys, tests, 562.
- Copper:** arsenic content, effect on conductivity, 693, 694.
 arsenical: analyses, 769.
 before and after gassing, photomicrographs, 768, 769.
 resistance to deterioration, 774.
 chemically pure, desirability, 696.
 coalescence, discussion, 773-774.
 conductivity and ductility tests: conclusions, 692.
 discussion, 692-699.
 results: curves, 682, 683.
 data, 688, 689, 691.
 lead content, effect, 684, 693.
 oxygen content, effect, 682.
 tin content, effect, 685.
 tin and lead: added, effect, 680.
 residual, effect, 687.
 specimens: analyses, 699.
 photomicrographs, 684-687, 690, 691.

- Copper: conductivity and ductility tests: specimens: preparation, 680.
 crystal, ion-electron lattice, 649, 650.
 deoxidation: arsenic effect, data, 704.
 discussion, 767.
 depth: effect of time and temperature: curves, 771.
 data, 756.
 photomicrograph, 765.
 oxygen-content effect: curve, 766.
 data, 762, 764.
 discussion, 759, 762.
 rate: effect of time and temperature, curves, 755.
 data, 756, 759.
 retardation, with depth, 767.
 reducing gases used, analysis, 755.
 tests: conclusions, 755.
 hydrogen, data, 764.
 results, discussion, 757, 770.
 specimens, analyses, 761, 764.
 deoxidised: need for specifying, 771.
 purity, effect, data, 757.
 distribution, New Cornelia ore, 75.
 Copper, electrolysis: see *Electrolysis*; *Electrolytes*.
 embrittlement, by hot reducing gases: causes, 744.
 effect, photomicrographs, 747.
 examples, 746-750.
 lack at very high temperatures, 773.
 prevention by annealing: photomicrographs, 777-781.
 tests: 779.
 conclusions, 782.
 etching reagents, use, 731-736, 741.
 exposure to hydrogen, safe temperature, 772.
 gas in, symposium, introduction, 742.
 hard and soft, deoxidation, data, 758.
 hardness: see *Meyer's analysis*, ball indentation test.
 heating, coalescence, 741.
 impurities, effect on properties, 693.
 leaching: collection, 33.
 costs, 53.
 harmful effect of iron, 36.
 leaching: "iron" phenomena, discussion, 44-45.
 see also *Ohio Copper Co. mine*.
 "life" of project, determination, 37.
 microscopic structure: annealed, view, 729
 cast, description, 715.
 cast and worked, description, 719.
 cold-drawn, views, 720-724, 730, 734, 735.
 cold-rolled, views, 716, 717.
 description, 707, 739-740.
 hot-rolled, views, 718-719, 731-733.
 oxygen eutectic: description, 724.
 views, 715, 725-728.
 photomicrographs, 708-712.
 recrystallised, description, 720
 | recrystallized and worked, description, 722.
 precipitation: by scrap-iron, cost, 104, 105.
 effect on grade, 49.
 rate, factors, 48.
 percolating waters, purpose of, 39.
- Copper, electrolysis: precipitation: recovery: 81-55.
 effect of iron content, 57.
 volume of water, effect, 47.
 water and air for, factors, 34.
 precipitation plant, 48
 reduction and refining, committee, xii.
 removal from silver precipitate, 321.
 solubility in aluminum: 571.
 effect of impurities, 579.
 tests, description, 562.
 susceptibility to reducing gases, 772.
- Copper-alloys: heat treatment and annealing, methods, 562-564.
 see also *Aluminum-copper*; *Aluminum-copper-silicon*; *Brass*; *Bronze*; *Piston alloys*.
- Copper-aluminum alloys: annealing: duration, effect, 572.
 photomicrographs, 572-573.
 structure, discussion, 574.
- Copper-aluminum diffusion alloy, photomicrograph, 1156.
- Copper balance, Inspiration Cons. Copper Co., leaching tests, 72
- Copper blast-furnace slags, impurities, removal, 28-30.
- Copper blister, impure, electrolytic refining, 134.
- Copper castings: exudations: cause, 704.
 effect on rolled copper: 705.
 photomicrographs, 705.
 oxide segregation between grains, view, 701.
 photomicrographs, 701.
 sections, photomicrographs, 702-704.
 structure, 701.
- Copper cement: see *Cement copper*.
- Copper concentrates: see *Ohio Copper Co. Lark, Utah*.
- Copper-cuprous oxide eutectic: description, 724.
 photomicrographs, 715, 725-728.
- Copper drillings: ignition in carbon dioxide: apparatus, sketch, 791.
 data, 790, 791.
- Copper nitrate solution: conductivity: 108-110.
 curves showing, 109, 110.
 reaction, equations, 110.
- Copper orebody, caving for leaching, 54.
- Copper ores: mixed: definition, 58.
 ferrie sulphate leaching: see *Inspiration Cons. Copper Co.*; *New Cornelia Copper Co.*; *Ohio Copper Co. mines*.
 solubility in water, 42.
- Copper oxide, in annealed copper bar, photomicrograph, 661.
- Copper photographic specimens, surfacing methods, 736.
- Copper rod, embrittlement, cause, 772.
- Copper sulfate: flotation of sulfides, effect, 360-361.
 see also *Ohio Copper Co. mine: leaching old workings*; *Silver, leaching*.
- Copper tailings: leaching tests, 55.
 recoverable copper, factors, 56.
- Copper-tin alloys, structure, photomicrographs, 1158, 1164.

- Copper-tin diagrams: comparison, 1162.
development, 1161.
sketches, 1159, 1162, 1163.
- Copper tubes: deoxidation tests, analyses, 761.
oxygen distribution, photomicrographs, 760.
- Copper wire, embrittlement during enameling, causes, 749.
- Copper-zinc diagram: development, 1166.
sketch, 1165.
- Copper-zinc-tin diagram, sketch, 1167.
- Coral sand, as blast sand, 448.
- Core Drilling in Geologic Exploration as Applied in Wyoming and Montana* (BARTRAM and WILSON), xix.
- Core Drilling Technology* (LONGYEAR, DONOVAN, ELLIOTT, BROWN), xxiii.
- Corrosion of Pipe Lines and Protective Covering* (MCGREW), xxiii.
- Costs: see *Crushing: Leaching, copper workings; Sands, mining; Standard Reduction Co. mill; Utah Copper Co.; Consolidated Mercur Gold Mines Co.*
- Cottrell treaters, lead blast-furnace fumes, use, 190-193.
- COYLE, F. B.: *Discussion on: Modification and Properties of Sand-cast Aluminum silicon Alloys*, 619-620.
- Cracking: see *Nickel silver.*
- Cracking of the Nickel Silvers in the Course of Annealing* (JONES and WHITEHEAD), xx, 834; Discussion, 849.
- CRANE, G. W.: *Notes on Geology of Tintic District*, xviii.
- Cranes, electrolytic copper refining, 129, 130.
- CRAWSHAW, J. E., and FOLEY, F. B.: *Effect on Air Gap in Explosion System on Production of Neumann Bands*, xxvi, 948-963; Discussion, 964-967.
- Critical density, crusher feed, 313.
- Critical temperatures: see *Iron; Iron-tungsten alloys.*
- Cross Process* (CROSS), xxiii.
- CROSS, ROY: *Cross Process*, xxiii.
- Crucible melting, brass, difficulties, 830.
- Crude oil, open-hearth fuel, controlled combustion, data, 1068-1071, 1074, 1075.
- Crushers: coarse crushing, Magna plant, 215, 220.
see also *Ball mills; Dodge jaw; Hardings conical mills; Rod mills; Rolls; Symons disk.*
- Crushing, coarse: see *Magna plant.*
costs, discussion, 223, 340.
efficiency: computation: 295-300.
curves, 295-297, 300.
definition, 295.
Kick vs. Rittinger laws, discussion: 298.
feed, critical density, 313.
leaching copper ore, degree, importance, 62.
- Haultain's data, 260, 262, 263, 296, 297.
mass of feed, fine elimes in, effect, 313.
wet, feed dilution, effect, 314.
see also *Ball milling; Chief Consolidated plant; Heterogenous rocks; Homogenous rocks, roll products; Spring tensions; Stamp milling.*
- Crushing phenomena: investigation: conclusions: 253.
application, 286-300.
see also *Heterogenous works.*
- Crushing rolls, breakage of particles in, manner, 263.
- Crushing tests: see *Heterogenous rocks; Homogenous rocks; McGill University.*
- Crystal formation: analogy, 858.
by atoms, diagram, 854.
by blocks, diagram, 853.
- Crystallisation: controlling forces, 641.
diagrams, 637, 641, 642, 648.
- Crystals, microstructures, diagrams, 852-854.
- Current Theories of the Hardening of Steel Thirty Years Later* (SAUVEUR), xxvi, 859-908.
- Cyanide flotation: metallurgical, 371.
patents, 370.
reagents, patents, 354.
sulfides, 362.
tests: conclusions: 370, 376, 380.
bornite, 374.
chalcocite, 374.
chalcopyrite, 374.
galena: 361-362.
photomicrographs, 365-367.
pyrite: 362, 364, 374.
photomicrographs, 366-369, 377-379.
sphalerite: 362, 363.
photomicrographs, 366-372.
ore used, analyses, 355, 372.
procedure, 355-372.
reagents used, 362, 373.
results: curves, 356-361.
data, 362, 372.
summary, 380.
time of contact, curves, 360, 376.
see also: *zinc cyanide.*
- Cyanide process, fine grinding, need, 249.
- Cyanide salts, metallic, flotation, use, 371.
- Cyanide solution, flotation, inhibition, discussion, 370.
- Cyanogen compounds: see *Cyanide solutions.*
- DALBEY, G. E.: *Discussion on Effect of Zinc Oxide on the Formation Temperatures of Some Ferrous Slags*, 28.
- D. & R. G. W. R. R., Salt Lake shop, briquetting tests, copper concentrates, 51-53.
- Danford, M. O.: *Application of Mining Tax Laws to the Petroleum Industry*, xix.
- DANIELS, SAMUEL: *Effect of Reheating upon the Al-Cu-Ni-Mg and the Al-Cu-Fe-Mg (Piston) Alloys*, xxv, 479-504.
- DANIELS, SAMUEL and WARNER, D. M.: *Mechanical Properties of the Aluminum-copper-silicon Alloy as Sand Cast and as Heat-treated*, xxi, 464-478.
- DARBY, E. H.: *Discussion on: The Lead Antimony System of Hardening of Lead Alloys*, 540.
- DARBY, G. M.: *Discussions on an Investigation of Crushing Phenomena*, 314.
Estimation of Oxygen and Sulfur in Refined Copper, 797, 798.

- Data on Use of Loading Machines in Bituminous Mines* (BRIGET), xxvii.
- DAVIS, C. H.: *Discussion on Hardness of Copper and Meyer's Analysis*, 676, 677.
- DAVIS, J. A. and RICE, G. S.: *Mining Petroleum in France and Germany*, xxiv.
- DAY, R. B., BROOKS, B. T., KNAPP, A., and: *Economic Incidence of Cracking*, xxii.
- DEAN, R. S.: *Discussion on the Lead Antimony System and Hardening of Lead Alloys*, 529-535, 535, 539, 540.
- DEAN, R. S. HUDSON, W. E., and FOLGER, M. F., on hardening of lead-antimony alloys, 517.
- DEAN, R. S., ZICKRICK, LYALL and NIX, F. C.: *The Lead Antimony System and Hardening of Lead Alloys*, xxv, 505-529.
- Decantation: washing sand and gravel: 427, 428 apparatus, 427, 428.
- Deck rivet, structure, photomicrographs, 1150.
- DECKER, E. J.: *Discussion on Modification and Properties of Sand-cast Aluminum-silicon Alloys*, 620.
- Dederich tunnel: see *Ohio Copper Co. mine*.
- Deep Hole Prospecting at Chief Consolidated Mine (DOBDEL) xviii.
- DE GOLYER, E. L.: *World Production of Petroleum in 1925*, xxii.
- DEJEAN, P., on harding of steel, 863, 865, 868, 871, 890.
- DELAYAN, N. B.: *Investigation into the Cause of Breakage in Crude Pipe-line Transportation Systems*, xxiii.
- Deoxidation: see *Copper*.
- Deoxidizer, rimmed steel, use, 1035, 1041.
- Department of Agriculture, restrictions on sand shipments, 382.
- DERN, G. H.: *Discussion on Chloridizing Mill of the Standard Reduction Co.*, 339.
- Development of Differential Flotation on Complex Sulfide Ores (BOOTH), xviii.
- Devitrification, glass sands, prevention, 402.
- DIEFFENBACH, E. E.: *Discussion on the Conductivity of Electrolytes Used in the Electrolytic Separation of Gold and Silver*, 121, 122.
- Directors, A. I. M. E., 1926-1927, xi.
- Discussion of Theory of Mine Ventilation (CALLEN), xxiv.
- Distillation by Pipe Stills (PRIMROSE), xxiii.
- DIX, E. H. JR.: *Discussion on Microstructure of Aluminum*, 626-627.
- DIX, E. H. JR and RICHARDSON, H. H.: *Equilibrium Relations in Aluminum-copper Alloys of High Purity*, xxv.
- DOBDEL, CHARLES: *Deep Hole Prospecting at Chief Consolidated Mine*, xviii.
- Dodge breaker, crushing tests, 263, 309.
- DONOVAN, P. W. and LONGYEAR, R. D.: *Core Drilling Technology: Diamond Drilling*, xxiii.
- Doré, selenium in, removal, 122.
- Dorr classifiers: bowl: tests: comparison with cones and straight type, 239-243, 248. flow sheet, 241, 242. results, 241, 242.
- Dorr classifiers: straight type: tests: comparison with cones and bowl classifiers, 239-243. flow sheets, 241 results, 241 use, Geduld mill, 243.
- Drilling Wildcat Wells in Wyoming (SINCLAIR), xix.
- Drills: see, *Rock drill*.
- Drossing: see *Lead smelting*.
- Drying: glass sands, methods, 417. industrial sands, methods, 437. Sperry process, 164.
- Dubbs Process (EGLOFF), xxiii.
- Ductility: see *Copper, conductivity and ductility tests*.
- Dumper, Magna plant, description and use, 213-215.
- Dust collection: electrostatic mill, method, 350. reverse nozzle, description and use, 91. roaster gas, 88.
- Dwight-Lloyd sintering machine: description and use, 177. flue dust and fume, treatment, 192.

E

- East Chicago, Ind.: see *Electrolytes, gold and silver separation*.
- EAVENSON, H. N.: *Report of Coal and Coke Committee*, xxvii. *Report of Sub-committee on Coal Mining to Committee on Ground Movement and Subsidence*, xxvii.
- Economic Design of Mine Airways* (RICHARDSON), xxiv.
- Economic Effect of Anti-knock Motor Fuels* (CLAYDEN and HORNING), xxiii.
- Economic Effect of Basic Changes in Refinery Operation* (W. MILLER), xxiii.
- Economic Incidence of Cracking* (BROOKS, DAY and KNAPP), xxiii.
- EDELNAU, L.: *Liquid Sulfur Dioxide Process*, xxiii.
- Effect of Air Gap in Explosion System on Production of Neumann Bands* (FOLEY and CRAWSHAW), xxvii, 948, Discussion, 664-967.
- Effect of Annealing upon the Hardness of Cold-worked Ingot Iron* (CLAYTON), xxvi, 926-928.
- Effect of Cyanogen Compounds on Floatability of Pure Sulfide Minerals-I* (TUCKER, and HEAD), xix, 354; Discussion, 370-371.
- Effect of Lead and Tin with Oxygen on the Conductivity and Ductility of Copper* (PILLING and HALLIWELL), xxvi, 679; Discussion, 692-699.
- Effect of Reheating upon the Al-Cu-Ni-Mg and the Al-Cu-Fe-Mg (Piston) Alloys* (DANIELS), xxv, 479-504.
- Effect of Zinc Oxide on the Formation Temperatures of Some Ferrous Slags* (MANN), xxv, 3; Discussion, 28-30.
- EGLOFF, GUSTAV: *Dubbs Process*, xxiii.
- Electric furnace, melting brass, advantages, 830.

- Electric locomotives, Magna plant use, 213.
- Electric Shot-firing Experiments in Coal Mines* (WATTS), xviii.
- Electrical equipment, Sperry process, 167.
- Electrodes, stripping, Nichols series process, 137.
- Electrolysis: cathode, impregnation with paraffin, 120.
- copper: development, history, 124.
- Nichols process: advantages and disadvantages, 144-145.
- anodes: description, 127
- preparation and handling, 127-130.
- silver content, importance, 144.
- busbars, 132.
- cathodes, painting, 128.
- concrete tanks, 130.
- lining, 130.
- description, 126.
- electrodes, stripping, 137.
- equipment, description, 126-131, 136.
- flat-bulb tank light, 136.
- flexibility, reasons, 134, 141.
- glue in electrolyte, 135.
- impure blister, refining, 134.
- installation cost, 132, 142.
- labor saved, 142.
- loading cranes, 129, 130.
- power: consumption, 131, 141, 144.
- saving, 144.
- supply, 133.
- silver and gold loss, 133, 142-144.
- series system, comparison with multiple system, 123, 144, 155.
- copper solutions, versus cementation, 85, 98, 104-107.
- measuring and recording, terms, 118-119.
- precious-metal anodes content, ratio to percentage loss, 144.
- tanks, shallow versus deep, 142-144.
- voltage, effect of ferrous and ferric iron and free acid, 61.
- Electrolyte: alumina in, effect, 61.
- constituents, effect on voltage, 61.
- "equal metal content" versus "equivalent concentrations," 118.
- glue added, effect, 135.
- gold and silver separation: ammonia in: cause, 110, 118, 119, 130.
- effect on conductivity: 111-113.
- curves showing, 112.
- effect on crystal formation: 113-117.
- photomicrographs, 115-116.
- composition, 109, 111, 114.
- conductivity: determination, 108.
- comparison, 119.
- curves showing, 109, 110.
- maximum, 117.
- potassium nitrates effect, 120.
- sodium nitrate effect, 120.
- conductivity tests: conclusions, 117.
- results, 114.
- nitric acid reaction with impurities, 120.
- Electrolyte tanks: shallow: discussion, 141-144.
- specific gravity, 111, 114.
- Electrolyte tanks: "grams per liter," conversion to "fractional normality," 119.
- requirements, 118.
- see also *Alumina*.
- Electrolytic cells: electrolysis of white lead: construction: 152-156.
- view, 154-156.
- Electrolytic precipitation, leached copper solutions, 59.
- Electrolytic white lead: see *Sperry process*.
- Electrons: see *Atomic structure*.
- Electrostatic mill: see *Midvale, Utah*.
- Elimination of Metalloids in the Basic Open-hearth Process* (KEATS and HERTT), xxvii, 1079; Discussion, 1106.
- ELLIOTT, J. E.: *Core Drilling Technology: Special Type Drills*, xxiii.
- Embrittlement: see *Copper*.
- Embrittlement of Copper by Hot Reducing Gases*. (FULLER), xxvi, 744; Discussion, 750-754.
- Employee Ownership in Industry* (SHAW), xxvii.
- Enameling, copper wire, embrittlement, causes, 749.
- Endurance Properties of Non-ferrous Metals*; (MCADAM, JR.), xx.
- Endurance Properties of Non-ferrous Metals-I* (MCADAM, JR.), xxv.
- Engine sand: photomicrographs, 440.
- properties and uses, 438.
- Equilibrium, chemical: see *Open-hearth process, basic*.
- Equilibrium conditions: see *Carbon; Manganese; Open-hearth Process; Phosphorous*.
- Equilibrium diagram: aluminum-copper alloys, 567.
- carbon-iron system, 853.
- iron-tungsten system, 970, 971.
- see also metals and alloys named.
- Equilibrium Relations in Aluminum-copper Alloys of High Purity* (DIX and RICHARDSON), xxv, 560; Discussion, 619-621.
- Error, probable, blast-furnace calculations, 1009.
- ESTABROOK, E. L. and RADER, C. M.: *History of Production of Salt Creek Field*, xix.
- ESTABROOK, E. L. and YOUNG, H. W.: *Waters of Salt Creek Field*, xix.
- Estimation of Oxygen and Sulfur in Refined Copper* (BASSETT and BEDWORTH), xxvi, 784; Discussion, 797-798.
- Etching, aluminum (piston) alloys, method, 485.
- Etching reagents, copper, 731-736, 741, 780.
- Eureka, Utah, volatilization mill at, 206.
- Eutectic temperatures: see *Aluminum-copper alloys*.
- Eutectoids: see alloys named.
- Evaluation of Coal* (SWEETSER), xxvii.
- Evaporation Losses in Storage and Transportation* (WIGGINS), xxiii.
- Evolution in the Preparation of Ores for Lead Blast Furnaces* (JESSUP), xviii.
- Explosibility of Coal and Other Dusts in a Laboratory Steel Dust-gallery* (ALLISON), xxvii.
- Explosion air-gap: see *Neumann bands, formation*.
- Explosives symposium, papers, xxvii.

Exudations on Copper Castings (BASSETT and BRADLEY), xxvi, 700; Discussion, 706.

Eye-pieces: see *Quartz eye-pieces*.

F

Factors Affecting the Cracking of Petroleum (PARMELEE), xxiii.

Feed sizes: see *Homogeneous rocks*.

Feeders: lead-ore roasters, 175.

sintering machines, description, 177.

Feeding, brass molding, discussion, 832.

FIELD, A. L. *Discussion on Making Rimmed Steel*, 1045.

Ferric chloride, as etching reagent, 731.

Ferric chloride solutions, leaching, corrosion, 101.

Ferric iron, by anodic oxidation, cheapness, 98.

Ferric oxide, open-hearth slag, variation, curves, 1083, 1086.

Ferric sulfate: as solvent agent, copper ore, 60
conversion of ferrous sulfate by SO_2 : equation, 101.

patents, 101.

from SO_2 and air, early work, 85-86, 98, 101, 103.

regeneration in non-diaphragm cell, 60.

Ferric sulfate and sulfuric acid: commercial:
gas for, content, 87.

small-scale tests, equipment, 90-92, 95.

units: costs, 96, 98-101, 104-107.

design, factors, 95.

size, 96.

dilute, aeration costs, 100, 104.

electrolysis vs. cementation, 85, 98, 104-107.

end reactions, equations, 89.

ferrous sulfate solution, iron content, 86.

from roaster gas: B. of M. process: aerator:
clogging, tests, 88.

application, 84, 94.

description, 91.

"Duro" cloth: life, 93.

use, 88.

gas bubbles: coalescence, remedy, 90, 95.
size, 86, 89-90.

pilot plant: see below under *semi-commercial tests*.

plant and synthetic solutions, data, 94.

reverse-nozzle dust collector, use, 91.

semi-commercial tests, data, 92-94.

tests: data, 87.

summary, 97.

types, 89.

recommended, 97.

views, 91, 92.

Ferric sulfate leaching: see *Inspiration Cons. Copper Co.*

Ferric sulfate solutions, leaching, corrosion, 101.

"Ferris-wheel" casting machine, description, 141.

Ferrite: as zinc-carrying slag ingredient, 29.

banded, in carbon steel, photomicrograph, 945.

examples, photomicrographs, 1149, 1159.

free: formation, microstructure, discussion, 855.

ultra-violet selective characteristics, 924.

Ferrosilicon, open-hearth charge, analyses, 1105.

Ferrous oxide, open-hearth slag, variation, curves, 1083, 1086.

Ferrous slag: formation temperatures: curves, 14-15.

data, 19-27.

determination, 7-8.

effect of zinc oxide on, 3-30.

tests: analyses: 19-27.

reliability, 28.

conclusions, 18.

determination, 11-12.

furnace: atmospheric conditions, 12-13.

description, 8-11.

operation, 12.

section, 11.

temperature possible, 9.

views, 9, 10.

measurements, means, 13.

temperature range, 13-16.

tests: Seger cones: behavior, 13.

bonds, 7.

materials, 7.

mounting, 9.

protection on removal from mold, 8.
solution required, 8.

high-zinc, effect of sulfur, 28.

impurities, removal, 28-30.

viscosity during fusion, 16.

FERTKE, C. R., photomicrograph by, count of grains and grain size, 304-306.

American Glass Sands, Their Properties and Preparation, xxv, 398-422.

Discussion on American Glass Sands, Their Properties and Preparation, 422.

FIELDNER, A. C. and SELVIG, W. A.: *Relation of Ash Composition to the Uses of Coal*, xxvii.

Film water, use in leaching, advantages, 35.

Filter cake: bridge of particles, formation, 227, 233.

structure: description and sketch, 227.

effect of amount of vacuum on, 227, 234-235.

Filter cloth, open weave, advantages, 225.

Filter opening: calculation, 232.

size and density of pulp particles, relation:
curves showing, 230-232, 234.

data, 228.

discussion, 226, 231.

Filter sand: photomicrographs, 438, 439.

properties and uses, 437.

Filter thickener: use, 236-238.

versus gravity thickener, 236-238.

Filters: solids in pulp, concentration, effect, 225.
see also *Moore filter*.

Filtration: high pressures, effect, 235.

mechanism, discussion, 225-234.

principles, 225.

pulp particles: arrangement: effect of concentration of solids, 232.

tendency, 225.

size, effect on bridge formation, 233.

pulpe: thickness, desirability, 234.

see also *Filter openings*.

seepage effect, discussion, 226.

- Filtration: washing sand and gravel, 426.
apparatus, 427.
see also *Sand filtration*.
- Fines: see *Sintering*.
- Fire clays, physical properties, 392.
- Fire cracking: see *Nickel silver, annealing cracking*.
- Fire cracks, nickel silver, photomicrographs, 839, 840.
- Firing, sintering charge, lead smelting, 180.
- FITZGERALD, CHARLES: *Transportation of Petroleum*, xxiii.
- Flat-bulb light, for examining electrolyte tanks, 136.
- Flooring sand, properties and uses, 445.
- Flotation: see *Cyanide solutions, flotation agents*.
- Flotation Development and Simplification at the Ophir Hill Consolidated Mill (LEMKE)*, xviii.
- Flotation mill, zinc-recovery tests, results, 351.
- Flotation oils and reagents, 353.
- Flow sheet: Inspiration Cons. Copper Co. leaching tests, 74
volatilization plant, 203, 205-208.
- Flue dust: definition, 190.
lead blast-furnace, retreatment and recovery, 190-197.
- Fluorspar, rimmed-steel manufacture, use, 1030, 1037.
- FOHS, F. J.: *Review of American (Petroleum) Production*, xxiii.
Technologic Progress in the Oil Industry, xxiii.
- FOLEY, F. B.: *Amorphous Cement and the Formation of Ferrite in the Light of X-ray Evidence*, xx, 850-857.
Discussion on Effect of Air Gap in Explosion System on Production of Neumann Bands, xxvi, 964, 965, 966, 967.
- Foley, F. B. and Crawshaw, J. E., *Effect of Air Gap in Explosion System on Production of Neumann Bands*, xxvi, 948-963; Discussion, 964, 967.
- FOLEY, F. B., CLAYTON, C. Y., REMMERS, W. E.: *Influence of Temperature, Time and Rate of Cooling on Physical Properties of Carbon Steel-II*, xxvi, 929-947.
- FOOTE, A. B. and FULTON, J. A.: *Mining Methods in Grass Valley District*, Calif., xxvii.
- FOOTE, P. D.: *The Relation between Metallurgy and Atomic Structure*, xxv, 826-656.
- Forecasting Petroleum Production (SANDS and OSBORN)*, xxiv.
- Formation temperatures: see *Ferrous slags*.
- Formulae: see *Tensional stress*.
- Foundry, iron, committee, xiii.
- Foundry sand; see *Albany, Lumberton and Millville sands*.
- Fractionation (PETERS), xxiii.
- FRASER, THOMAS, and YANCY, H. F.: *Air Sand Process of Cleaning Coal*, xxvii.
- FREEDMAN, LOUIS: *Gulf Coast (Petroleum Production)*, xxiv.
- Fuel: see *Open-hearth furnace*.
- FULLER, T. S.: *Embrittlement of Copper by Hot Reducing Gases*, xxvi, 744-750.
- FULLER, T. S.: *Discussion on Action of Reducing Gases on Heated Copper*, 773.
- FULTON, J. A. and FOOTE, A. B.: *Mining Methods in Grass Valley District*, Calif., xxvii.
- Fume: definition, 190.
lead blast-furnaces, retreatment and recovery, 190-197.
- Furnace-bottom sand, uniformity, 390.
- Furnaces: speed, effect on slag formation, 28.
see also *Electric furnaces; Ferrous slags, formation temperature tests; Holt-Dern furnaces; Lead blast-furnaces; Roasting furnaces; Wire-bar*.
- Fusion temperatures: determination; 969.
hood, view, 969.
- G
- GALE, H. S.: *Borate Deposits near Kramer, Calif.*, xxv, 449-463.
- Galena: roll-crushed, screen analyses, logarithmic plots, 258, 259.
silver-bearing, recovery, 342.
see also *Cyanide solutions, flotation tests*.
- GALLOWAY, J. J., *wear tests by, discussion*, 265.
- Gamma iron: arrangement of atoms, diagrams, 852
solubility of carbon in, 1146.
- GARFAS, V. R. and WHEITSEL, R. V.: *Mexican Oil Fields*, xxiv.
- Garfield Utah, copper smelter, A. I. M. E. trip, xvii.
- GARNER, A. H.: *Suggested Nomenclature and Correlation of the Geological Formations in Venezuela*, xxiv.
- Gas in copper, symposium, introduction, 742.
- Gasoline Problem (HOLMES)*, xxiii.
- Gasoline shovels, mining sand, use, 384.
- GATES, J. F., TUCKER, E. L. and HEAD, R. E.: *Effect of Cyanogen Compounds on the Floatability of Pure Sulfide Minerals.-II*, xix, 372-380.
- Gating, brass molding, discussion, 832.
- GAUDIN, A. M.: *Investigation of Crushing Phenomena*, 253-310.
Discussions on: Classification in Witwatersrand Mills, 251, 252.
Investigation of Crushing Phenomena, xxv, 311, 312, 314-316.
- Geduld Proprietary Mines, mill: classification tests: feed, quality, 245.
flow sheets, 240-242.
results: bowl type, 242.
cones, 240.
straight type, 241.
installation, flexibility, 243.
practice, flow sheet, 243-244.
straight type Dorr classifiers, use, 243.
- GEIS, W. H.: *Billy Creek Field*, xix.
- Genter filter-thickener, use, 236-238.
- Geology: see *Mining geology*.
- GEORGE, H. S., *Discussion on Introduction to Ultra-violet Metallography*, 924-925.
- German peritectic brass, analysis, 800.
- GESTER, G. C. and WAGY, E. W.: *California (Petroleum Production)*, xxiii.

- Glass sands:** batch soum, formation, 407.
composition, 398-399.
devitrification prevention, 402.
grades, specifications, 400.
grading methods, 418.
grains: shape: discussion, 410.
views, 410-412.
sizes: limits, 408.
uniformity, importance, 406.
impurities, occurrence and effect, 401-406.
mining and preparation: methods and equipment, 414-420.
views, 414.
occurrence, 398.
prices and production, 422.
quarry, 415.
tolerances, 400.
washed, screen tests, results, 409.
- Glue, in electrolyte, 135.**
- Godfrey roasters:** lead ore: description, 174.
operation, 174-177.
- Gold:** accumulation in classifier circuit, 248, 250.
concentrating recoveries, 351.
crystal, ion-electron lattice, 649, 650.
loss, Nichols series process, 133, 142-144.
recovery, volatilization process, 209.
- Gold and silver separation:** see *Electrolytes*.
- Gold-bearing pyrite, recovery, 342.**
- Gold ore, Witwatersrand, grinding, size, 250.**
- Goodrich, H. C.: Shovel Operations at Bingham Utah Copper Co., xviii.**
Discussion on Recovery of Copper by Leaching, Ohio Brass Co. of Utah, 56, 57.
- Graham, Thomas, on colloid characteristics, 906.**
- Grain-growth loss: see Metals.**
- Granite:** Stony Creek, jaw crusher product, screen analyses, logarithmic plot, 264.
Stony Point, roll-crushed, screen analyses; logarithmic plot, curve, 258.
- GRANT, J. E. and others: Treatment of the Telluride-bearing Gold Ores of the Wright-Hargreaves Mines, Ltd., xxv.**
- Granville Springs, glass sands, grades, 419.**
- Graphic Method of Work Done by Producing Wells (LINDSAY), xix.**
- Graphite: see Anodes.**
- Gravel:** classification, 432.
impurities, removal, 424, 430-431.
sizing, methods, 431-433.
washing: methods, 426-431.
water, amounts, 428.
uniform feed, importance, 429.
- Gravity concentrator, description and use, 342.**
- Gravity thickener, vs. filter thickener, 236-238.**
- Great Capaon, glass-sand quarry, 415.**
- Greenawalt reducers, use, comparison, 102-103.**
- GREENAWALT, W. E.: Discussion on Production of Ferric Sulfate and Sulfuric Acid from Roaster Gas, 101.**
- GRENET, G., on harding of steel, 865, 890.**
- Griszlies, Magna plant, view, 218, 219.**
- GROSSMANN, M. A.: Discussion on Iron-tungsten System, 1008.**
- Ground movement and subsidence, papers, xxvii.**
- Growth loss, metal grains, 1138.**
- GUILLET, L.: on hardening of steel, 865, 868, 871, 893.**
- Gulf Coast (Petroleum Production) (FREEDMAN), xxiv.**
- Gun metal; heat treatment, 1172.**
- Gun metal photomicrographs, 1169.**
- GUNDEROTE, C. J.: Discussion on an Investigation of Crushing Phenomena, 314.**
- ## H
- HAAS, FRANK: Report of Sub-committee on Coal-mine Ventilation, xxiv.**
- HADFIELD, W. H.: on hardening steel, 863, 866, 868, 871, 893, 969.**
- HAIGHT, C. M.: Sharpening and Handling Drill Steels at Franklin, xxvii.**
- Halide-alkali crystals: see Atomic structure.**
- HALLIWELL, G. P.: Discussion on Annealing of Commercial Copper to Prevent Embrittlement by Reducing Gases, 782-783.**
- HALLIWELL, G. P. and PILLING, N. P.: Effect of Lead and Tin with Oxygen on the Conductivity and Ductility of Copper, xxvi, 679-692.**
- HANEMANN and SCHRAMER, work by, 904.**
- HANLEY, H. R.: Discussion on Chloridizing Mill of the Standard Reduction Co., 338.**
- HANSEN, C. A.: Discussion on Mining and Preparation of Eastern Molding Sands, 391-393.**
- Hardening: see Lead-antimony alloys; Lead-antimony-tin alloys; Steel; Troostite.**
- Hardinge conical mill, crushing tests, 285.**
- Hardness: colloid factor, 905.**
definition, 905, 908.
tests: ball vs. conical point, discussion, 674, 675.
log log plot, load-diameter relation, 662
see also *Aluminum-copper-silicon alloy; Iron, cold-worked ingots; Meyer's analysis, ball indentation test; Steel.*
- Hardness of Copper and Meyer's Analysis (HOYT and SCHERMERHORN) xxvi, 657; Discussion, 671-678.**
- HARRIS, F. W.: Discussions on: Action of Reducing Gases on Heated Copper, 772. Microscopic Structure of Copper, 741.**
- Hartz jigs: description and use, 343.**
plungers, stroke and speed, 344.
- HAULTAIN, H. E. T.: crushing efficiency curves, adaptation, 262, 263.**
data on crushing, efficiency, adaptation, curves, 296, 297.
data on manner of rock breakage, 260.
slow-motion pictures, breakage of rocks, conclusions, 260.
- Hayden process, electrolytic copper refining, development, 124.**
- HAYWARD, C. R.: Discussions on: Hardness of Copper and Meyer's Analysis, 676. Effect of Lead and Tin with Oxygen on the Conductivity and Ductility of Copper, 695-696.**

- HAYWARD, C. R.:** *Discussions on: Effect of Zinc Oxide on the Formation Temperature of Some Ferrous Slags* 28, 30.
Lead-Antimony System of Hardening Lead Alloys, 526-538.
- HEAD, R. E. and TUCKER, E. L.:** *Effect of Cyanogen Compounds on Floatability of Pure Sulfide Minerals*, I, xix, 354-370.
- HEAD, R. E., TUCKER, E. L., and GATES, J. F.:** *Effect of Cyanogen Compounds on the Floatability of Pure Sulfide Minerals*, II, xix, 372-380.
- Heat:** see *Open-hearth furnace*.
- HEATH, C. L. and others:** *Treatment of the Telluride-bearing Gold Ores of the Wright-Hargreaves Mines, Ltd.*, xxv.
- Heating temperature:** see *Oxygen in refined copper*; *Sulfur in refined copper*.
- Heating system, leaching solution**, 337.
- Heat loss, furnaces, causes and prevention**, 339.
- Heat treatment:** alloys: effect, 1168.
 curves, 1170, 1171.
 bronzes and brasses, 1172.
 see also *Aluminum-copper-silicon alloy*; *Piston alloys*.
- HENTON, H. M.:** *Pyro- and Hydro-treatment of Magnesite and Dolomite*, xxv.
- HERTY, C. H., JR.:** *Chemical Equilibrium of Manganese, Carbon, and Phosphorus in the Basic Open-hearth Process*, xxvii, 1107-1132.
Discussions on: Chemical Equilibrium of Manganese, Carbon and Phosphorus in the Basic Open-hearth Process, 1134
Probable Error in Blast-furnace Records and Calculations Therefrom, 1023.
- HERTY, C. H. JR.; and KEATS, J. L.:** *Elimination of Metalloids in the Basic Open-hearth Process*, xxvii.
- Heterogenous rocks:** crushed, logarithmic size-curves, 301-303, 308, 309.
 definition, 243, 254.
 discussion, 301.
 grains: size, average, 307.
 number and sizes, photomicrographs, 304-306.
 preferential breaking sizes; averages, tables, 305, 306
 tests, results, 304
 variation, curves, 308, 309.
 roll-crushing tests, results, 304.
 screening and sizing tests, description, 304.
- HIBBARD, H. D.:** *Discussions on: Effect of Zinc Oxide on the Formation Temperatures of Some Ferrous Slags*, 28.
Making Rimmed Steel, 1042-1043, 1046.
 on gases that form blowholes in rimmed ingots, 1032, 1042.
- HIERS, G. O.:** *Discussion on the Lead Antimony System of Hardening Lead Alloys*, 539.
- HILL, H. B.:** *Increasing Production by Shooting*, xxiii.
- HINTON, G. B.,** flotation of silver minerals in water, tests, 370.
- Hirst Institute of Metals, brass analysis**, 800.
History of Production of Salt Creek Field (ESTABROOK and RADDER), xix.
- HIXON, A. W., WORK, L. T., and ODELL, I. H.:** *Mechanism of Filtration*, xxv, 225-234.
- Holland Tunnel (New York-New Jersey), A. I. M. E. trip**, xxii.
- Holland Tunnel (Singstad)**, xxiv.
- HOLMES, J. A.:** *Shutting in Rangely Gas Well*, xix.
- HOLMES, R. C.:** *Gasoline Problem*, xxiii.
- Holt-Dern furnaces, description and operation**, 318.
- Holt-Dern roasters: description and use**, 332.
 fuel economy, 339.
 operation, 340.
 plan and section, 333.
 views, 334, 335.
 volatilization loss, prevention, 340.
- Homogeneous rocks: ball-mill product, particle breakage, manner**, 286.
- ball mill tests: continuous discharge:** 285.
 products, screen analyses, logarithmic curves, 285, 286.
 feed over critical size: duration: data, 283, effect, 280.
- batch ball mill: nip angle, relations, diagram**, 277.
- batch ball-mill product: ball size**, 284.
 breakage, 586.
 feed grain size: effect, 274.
 relation to ball size and nip angle, 277
 grain shapes, 278, 286.
 photomicrographs, 279, 282.
 screen analyses, logarithmic plots, 274-277, 280, 281, 283-284.
- breakage in rolls: discussion**, 260.
 sketch, 262.
- crushing efficiency, discussion**, 295-300.
 definition, 253, 254.
- jaw-crushed: particle breakage, manner**, 264.
 screen analyses, logarithmic plot, 263.
 shape of particles, 264.
 -200 mesh: area of surface: computation, 292-294.
 curves, 292, 293.
 average volume: computation, 294.
 curves, 294, 295.
 from crushing, observed and computed, comparison, data, 288.
 screening, discussion, 287.
 size, computation, 289.
- nip angle: explanation**, 277.
 relations, diagram, 277.
- particles: fineness possible**, 287.
 size, relation to percentage corresponding to a given size, 286-300.
- pebble-mill product, shapes, photomicrographs**, 266.
- pebble-mill wear test without pebbles**, 264.
- rod-mill product: particle breakage, manner**, 273.
 photomicrographs, 269.
 screen analyses, logarithmic plots, 270, 271, 273.
 size curves, 268.

- Homogeneous rocks: rod-mill tests: description, 268-274.
 number of rods used, effect, 272.
 roll-crushed, breakage of particles, manner, 263.
 feed sizes, relation to set of rolls, curves, 260.
 photomicrographs, 261.
 screen analyses: logarithmic plots: 256-259.
 discussion, 255-263.
 shape of particle, 263.
 size curves: 256.
 method of plotting, 255.
 wear tests: see *Quartz*.
- HONDA, KOTARO: on hardening of steel, 864, 866, 868, 869, 896.
- HOPKINS, E. B. and WASSON, H. J.: *Venezuela and the West Indies (Petroleum Production)*, xxiv.
- Hoppers, Magna plant, view, 218, 219.
- HORNING, H. L. and CLAYDEN, A. L.: *Economic Effect of Anti-knock Motor Fuels*, xxiii.
- HOWE, H. M.: influence in physical metallurgy, 1174.
 Memorial Lecture, *Last Twenty-five Years of Metallurgy*, xxvii, 1135-1178.
 steel hardening theory, 1145.
- HOYT, S. L.: *Discussions on: Effect on Air Gap in Explosion System on Production of Neumann Bands*, 964.
Hardness of Copper and Meyer's Analysis, 671, 674-678.
 on hardening of steel, 866, 868, 869, 871, 895.
- HOYT, S. L. and SCHERMEHORN, T. R.: *Hardness of Copper and Meyer's Analysis*, xxi, 657-671.
- HUBER, L. W.: *Operating Characteristics of Centrifugal Fans and Use of Fan Performance Curve*, xxiv.
- HUESSENER combustion regulator, section, 1066
- HUESSENER, K.: *Combustion in the Open Hearth Furnace with Special Reference to Automatic Control*, xxvi, 1047-1078.
- Huff concentrating machines: limitations, 350.
 use, 349.
- HUMFREY, M.: steel hardening theory, 1145.
- Hunt and Douglas process, reference, 98, 103.
- HUNTLEY, L. G.: *Columbia and Peru (Petroleum Production)*, xxiv.
- Hydraulic mining: molding sands: 384, 387.
 view, 386.
- Hydrogen: blowholes in rimmed steel: effect, 1032.
 views, 1032.
 deoxidation tests, data, 764.
 reduction apparatus, view, 785.
- Illinois: glass sand, occurrence, 419.
 industrial sands, occurrence, 434.
 see also *Ottawa, Ill.*
- Illuminating gas, as deoxidiser, analysis, 755.
- Impact tests: Al-Cu-Si alloy, 467.
 data, 476-478.
- Impact values, effect of quenching temperatures, 937.
- Improvements in the Series System of Electrolytic Copper Refining Recently Developed by the Nichols Copper Co. (MERRISS)*, xxv, 123; Discussion, 142-145.
- Increasing the Extraction of Oil by Water Flooding (UMPLEBY)*, xxiii.
- Increasing Production by Shooting (HILL)*, xxiii.
- Indiana: see *East Chicago*.
- Industrial relations, papers, xxvii.
- Industrial sands: preparation and use, research needed, 447.
 special: by-products, 446.
 definition, 434.
 mining and preparation, methods, 435.
 photomicrographs, 438-444.
 supply, sources, 343.
 uses and properties, 437.
 washed, analyses, 446.
 transportation, 437.
- see *Abrasive; Chemical; Engine; Filter; Flooring; Metallurgical; Moulding; Oxychloride cement-plasters; Potter's; Pulverising; Roofing; Sand-blast; Stand-ard; Stone-sawing sands.*
- Influence of Temperature, Time and Rate of Cooling on Physical Properties of Carbon Steel-II (FOLEY, CLAYTON and REMMERS)*, xxvi, 929-947.
- Inspiration Cons. Copper Co.: ferric sulfate leaching-tests: acid, amounts and costs, 80.
 anodes, choice, 60.
 anodes and cathode efficiencies, variation, control, 61.
 cathode, solubility in electrolyte, prevention, 72.
 cement copper in discard solution, dissolving, 72, 79.
 copper balance, 72.
 description, 63-71.
 electrolyte: alumina in, effect, 61.
 constituents, effect on voltage, 61.
 extraction, data, 64-70.
 heads, copper content, 64-69.
 laboratory conclusions, 62.
 lack of discard, problem, 80.
 ore sizes, 61-63.
 precipitation, method, 59.
 problems, discussion, 59-62.
 purpose, 58.
 results: data, 64-70.
 discussion, 63-71.
 solvent agent, 60.
 tails, copper content, 64-69.
 tank-house data, 70.
 washing method, 68.
 leaching: experiments, history, 82-83.
 methods, comparison, 74-80.
 solutions, acidity, 100.
 ore, accessibility to solutions, 62.
 ores tested, copper content, 59.
 pilot plant: description, 71.
 flow sheet, 74.

- Institute of Metals: annual lecture, 628-656.
committee, xiii.
papers, list, xx, xxv.
- Inter-crystalline brittleness: see *Metals*.
- Inter-crystalline cement, amorphous, criticism of theory, 855.
- International Smelting Co. plant, Salt Lake City, equipment, 174.
- Inter-strain theory, steel hardening, 1145.
- Introduction to Ultra-violet Metallography* (LUCAS), xxvi, 909; Discussion, 924-925.
- Investigation into the Cause of Breakage in Crude Pipe-line Transportation Systems* (DE-LAVAN), xliii.
- Investigation of Crushing Phenomena* (GAUDIN), xxv, 253; Discussion, 310-316.
- Inwood limestone: breakage, 310.
logarithmic size-curves, 308, 309.
- Iron: cold-worked ingot: hardness: effect of annealing: curves, 927.
data, 926, 928.
discussion, 926.
test specimens, view, 927.
consumption, leaching copper solutions, 56.
effect in: aluminum brass, data, 824.
aluminum silicon alloys, 582, 583, 587.
brass, 810.
photomicrographs, 813-815.
on modified aluminum-silicon alloys, 598, 602.
on recovery of copper in leaching, 57.
flotation oils and reagents, 353.
in aluminum-silicon alloys, limit, 619.
introduction into brass, method, 811.
in troosite, condition, 878.
precipitation with, 59.
leached copper, consumption, 50.
pure: critical temperatures, 985.
hardness, increase, cause, 1006.
millivolt readings, 985.
scrap, for precipitation, cost, 104, 105.
solubility: see *Neumann bands*, effect.
structures, ultra-violet selective characteristics, 924.
see also *Alpha iron*; *Gamma iron*; *Ferric oxides*; *Ferrous oxides*; *Martensite*; *Wrought iron*.
- Iron alloys, aluminum base: see *Piston alloys*.
carbon-free, hardness, 1006.
see also *Aluminum-iron-silicon alloys*.
- Iron and carbon, in martensite, bond, 865.
- Iron and nickel: see *Aluminum brass*.
- Iron and steel: committees, xiii.
mechanical treatment, committee, xiii.
papers, list, xviii, xxvi.
- Iron blast-furnace slags, impurities, removal, 30.
- Iron-carbon diagram: development, 1141.
sketch, 1142.
- Iron Fields of the Iron Springs and Pinto Districts, Iron County, Utah* (MACVICHIE), xviii.
- Iron-nickel diagram, sketch, 1144.
- Iron-nitrogen diagram sketch, 1151.
- Iron ore: moisture, variability, 1018.
silica in, variation, 1021.
- Iron-ore committee, xiii.
- Iron oxide, content: ferrous-slugs, 19-27.
reliability, 28.
glass sands, occurrence and effect, 403.
open-hearth slag, formation, 1109.
replacement by zinc oxide, slag-formation temperatures, 13-17.
- "Iron" problem, copper leaching, possible solution, 44.
- Iron-ton, Utah, A. I. M. E. trip, xvii.
- Iron-tungsten alloys: carbon in; effect; 1004.
photomicrographs, 1004, 1005.
cooling curves, 984.
critical temperatures, 985.
discussion, 1002.
grain size, effect of tungsten content: 989, 1003.
photomicrographs, 986.
hardness: effect of aging: curves, 991-994.
data, 994, 995.
discussion, 991, 1003.
effect of tungsten content, 986, 989, 1003.
measurements, 990.
millivolt readings, 985.
photomicrographs, 972-983.
physical properties: effect of aging: curves, 999-1001.
data, 1001.
discussion, 999.
tungsten content, effect, 986, 989, 1003.
- Iron-tungsten-carbon steel, hardness, diagram, 1005.
- Iron-tungsten system: description, 1003.
equilibrium: diagram, 970-971.
discussion, 970.
- Iron-tungsten System* (SYKES), 968; Discussion, 1004-1008.
- Isochores, Van't Hoff's formula, 1108.
- JACOBSON, SIMON, SACKETT, B. L., BARDWELL, CARLOS, JENSEN, N. H. and: *Lead Smelting in Utah*, xviii, 171-197.
- JACKSON, P. W.: *Blast Furnace Plant of the Columbia Steel Corporation*, xviii.
- James Douglas medal, presentation, 1926, xxii.
- Jaw crushers: particle breakage, manner, 264.
-200-mesh material, computed, and observed, data, 288.
see also *Homogenous rocks*.
- JEFFRIES, ZAY: on hardening of steel, 863, 868, 870, 871, 897.
- JENKINS PROCESS (WELLING), xliii.
- JENSEN, N. H., SACKETT, B. L.: BARDWELL, CARLOS, JACOBSON, SIMON and: *Lead Smelting in Utah*, xviii, 171-197.
- JESSUP, D. W.: *Evolution in the Preparation of Ores for Lead Blast Furnaces*, xviii.
Discussion on Lead Smelting in Utah, 197.
- JOHNSON, FREDERICK, on oxygen-free versus "tough-pitch" copper, 724.
- JOHNSON, J. E. JR.: prize, award, 1926, xxii.
work of, reference, 30.
- JONES, E. L.: *Discussion on Mining and Preparation of Eastern Molding Sands*, 389.

J. and WHITEHEAD, E.: *The Annealing Cracking of the Nickel Silvers*, xx, 834-849.

JONES, J. L.: *Discussion on Modification and Properties of Sand-cast Aluminum-silicon Alloys*, 619.

JORGENSEN, E. L.: *Discussions on: Conductivity of Electrolytes Used in the Electrolytic Separation of Gold and Silver*, 123.

Improvements in the Series System of Electrolytic Copper Refining as Recently Developed by the Nichols Copper Co., 143.

JOSEPH, T. L.: *Discussion on Probable Error in Blast-furnace Record and Calculations Therefrom*, 1023.

K

Kansas-Oklahoma, (Petroleum Production) (McWHIRT), xiv.

KEATS, J. L. and HERTY, C. H. JR.: *Elimination of Metalloids in the Basic Open-hearth Process*, xxvii, 1079-1106.

KEIGLEY, C. T.: *New By-product Coke Plant of the Columbia Steel Corporation*, xviii.

KEMP, L. W. and ARCHER, R. S.: *Modification and Properties of Sand cast Aluminum silicon Alloys*, xxv, 581-619.

Kentucky, bentonite, source, 390.

KERN, E. F.: *Discussion on Conductivity of Electrolytes Used in the Electrolytic Separation of Gold and Silver*, 118, 120-122.

KERN, E. F., COLCORD, F. F., MULLIGAN, J. J. and: *Conductivity of Electrolytes in the Electrolytic Separation of Gold and Silver*, xxv, 108-117.

KEYES, H. E., OLDBRIGHT, G. L., WARTMAN, F. S., and: *Production of Ferric Sulfate and Sulfuric Acid from Roaster Gas*, xix, 84-98.

Keystone mine, A. I. M. E. trip, xvii.

Kick's law, mechanical efficiency, versus Rittinger's, 298.

KINNEY, C. L., JR.: Robert W. Hunt medalist, 1926, xxii.

Discussion on Making Rimmed Steel, 1044.

KINNEY, S. P.: J. E. Johnson, Jr. prize, 1926, xxii.

Kish, definition, 1090.

KLINGER, PAUL, on the nature of gases in live and killed steel, 1041.

KNAPP, ARTHUR: *Petroleum Statistics and the Economic Situation*, xiv.

KNAPP, A., BROOKS, B. T., DAY, R. B., and: *Economic Incidence of Cracking*, xxiii.

KNOX, W. J.: *Cleaning Oil Wells by Heated Oil*, xix.

Kramer, Calif.: borate deposits: beds, description, 454-548.

history, 453-459.

map, 455.

unaltered, significance, 451.

coemanite: deposits, origin, 450, 452.

specimens, description, 450.

KRAMPERT, E. W.: *Lost Soldier Oil Field*, xix.

L

LABBE, A. L.: *Application of the Cottrell Process in Lead and Copper Smelting*, xviii.

Labor, Nichols Copper Co. refinery, 142.

Ladle: see *Open-hearth, basic; slag*.

LAHRE, F. H.: *Texas Outside Gulf Coast (Petroleum Production)*, xxiv.

Lark, Utah: copper concentrate tailings, leaching tests, 55.

copper precipitation plant at, 48.

Last Twenty-five Years of Metallography—Howe Memorial Lecture—(CAMPBELL), xxvii, 1133-1178.

Lattice energies: see *Crystals named*.

Lattice structures, alpha and gamma iron, 852.

Laurel Hill, N. Y. C.: see *Nichols Copper Co.*

LAWS, E. H.: *Discussion on Lead Smelting in Utah*, 198.

LAWTON, V. O.: *Discussion on the Chief Consolidated Volatilisation Process and Mill*, 210.

Leaching: acid, costs, 78, 80.

film water versus mass percolation, 38-42. percolation, description, 319.

segregated unleached areas, causes, 78.

soluble in absorbing medium, equation, 37.

solubles, difficulty, 37.

water and time needed, determination, 37.

see also *Copper; Inspiration Cons. Copper Co., ferric sulfate leaching; New Cornelia Ohio Copper Co., Copper Co.; Sand filtration; Silver, leaching; Standard Reduction Co. mill; Water*.

Leaching Mixed Copper Ores with Ferric Sulfate; Inspiration Copper Co. (VAN ARSDALE), xxv, 58; Discussion, 74-83.

Leaching solutions, acidity, discussion, 100.

Leaching tanks, Standard Reduction Co. mill, 334.

Lead: antimony in, solubility, 507.

concentrating, recoveries, 351.

drossing and casting, Utah practice, 187.

flotation oils and reagents, 353.

in copper, effect, 684, 693.

precipitation: see *Standard Reduction Co. mill*.

recovery, volatilisation process, 209.

reduction and refining, committee, xii.

removal from blast furnace, method, 187.

smelting: arsenic recovery, methods, 195.

baghouses, description, 192, 194, 195, 196.

blast-furnace matte, prercoasting, 176.

blast-furnace practice: difficulties, 189.

Utah, 182-189.

cadmium recovery, method, 197.

calcination, Utah practice, 175, 177.

copper matte, blowing in converters, 195, 190-197.

drossing, practices, 198.

flue dust, and fume, recovery, Utah 197-199.

practice at Salida, Colo., 198.

prercoasting, Utah, 174.

sinter fines, treatment, methods, 180.

- Lead: smelting: sintering: pallet speed, 181.**
 sulfur problems, 180, 181.
 Utah practice, 177-182.
- Utah: early practice, 171-173.**
 mechanicalisation, 173.
 present plants, location and equipment, 173.
 see also *Anodes; Lead blast-furnaces.*
- volatilisation, 211.**
 white, electrolytic: see *Sperry process.*
- Lead and tin, in copper, effect, 680, 687.**
- Lead-antimony alloys: annealed: effect, photo-micrograph, 515.**
 tensile strength, data, 519.
 cast, tensile strength, 513.
 conductivities: effect of aging time, 512.
 measurement: 508.
 curves, 509-512.
 density curve, 510.
 hardening: annealing temperature: effect: 519.
 curves, 518.
 antimony content, effect, 523-525.
 heating time, effect, 518.
 mechanism, 535.
 quench rate: effect, 525.
 curves, 525, 526.
 rate and amount, factors, 519-526.
 speed: factors, 536.
 curves, 520-526.
 summary, 529.
 tests, conclusions, 528.
 particles, agglomeration, 512.
 photomicrographs, 511-515, 530-534.
 physical properties, investigations, 505.
 softening: high temperatures: data, 527.
 curves, 527, 528.
 solidification, reaction, 511.
- Lead-antimony system: equilibrium diagram: 516.**
 determination, method, 506-516.
 investigations, 505-516.
 peculiarities, 510.
- Lead-Antimony System and the Hardening of Lead Alloys (DEAN, ZICKRICK and NIX),**
 xxv, 505; Discussion, 529-540.
- Lead-antimony-tin alloys: hardening tests: curves, 537-538.**
 conclusions, 537.
 data, 536-537.
- Lead-blast-furnace, matte: handling, 185.**
 preroasting, 176.
- Lead blast-furnaces: charging, 183.**
 description, 182.
 dust catchers, description, 194.
 operation, 185.
 slag: analysis and handling, 185-187.
 impurities, removal, 28-30.
 permissible zinc-oxide content, 3-5.
 see also *Ferrous slags.*
 tapping floor, ventilation, 188.
- Lead-copper matte, blowing in converters, 195, 197-198.**
- Lead Smelting in Utah (SACKETT, BARDWELL, JACOBSON and JENSEN),** xviii, 171, Discussion, 197-199.
- Lead sulfate, solubility by sodium sulfate, 326.**
- Leadville, Colorado, district, low-grade zinc deposits, 6.**
- LE CHATELIER, H., on hardening of steel, 863, 866, 868, 871, 897, 1145.**
- LEITER, SUSAN B.: *Annealing of Commercial Copper to Prevent Embrittlement by Reducing Gases*, xxvi, 776-782.**
- LEMKE, C. A.: *Flotation Development and Simplification at the Ophir Hill Consolidated Mill*, xviii.**
 Milling Practice at Midvale, xix, 342-353.
- LESTER, H. H., on hardening of steel, 863, 866, 868, 870, 872, 898.**
- LEWIS, J. H.: *Discussion on Investigation of Crushing Phenomena*, 312-14.**
- Lignite, removal from sand and gravel, 430.**
- Lime: in ferrous slags tested, content, 19-27.**
 in glass sands, occurrence and effect, 404.
 replacement by zinc oxide in slag, 13-16.
 solution from limestone, open-hearth charge, rate, 1095.
- Lime and sodium carbonate, flotation of sulfides, effect, 356, 357, 359.**
- Lime boil: see *Open-hearth process.***
- Limestone, solution of lime from, open-hearth charge, rate, 1095.**
- LINDSAY, J. C.: *Graphic Method of Work Done by Producing Wells*, xix.**
 "Line loss," electrolytic copper refining, prevention, 132.
- Lining: see *Open-hearth furnace.***
- Liquid Oxygen as an Explosive* (O'NEILL and VAN FLEET), xxvii.**
- Liquid Sulfur Dioxide Process* (EDELEANU), xxiii.**
- Lithium bromide crystal, lattice energy, compressibility and pressure coefficient, 646.**
- Lithium chloride crystal, lattice energy, compressibility, and pressure coefficient, 646.**
- Lithium fluoride crystal, lattice energy, compressibility, and pressure coefficient, 646.**
- Lixiviant: see *Solvent agent; New Cornelia Copper Co.***
- LOCKE, C. E.: *Discussions on: Classification in Witwatersrand Mills*, 250.**
 Crushing Phenomena, 315.
 Mechanism of Filtration, 238.
- Locomotives: see *Electric locomotives.***
- LOGAN, W. N. and others: *Mississippi Valley Field, (Petroleum Production)*, xxiv.**
- Logarithmic size-curves, 301-309.**
 interpretation, 310.
 method of plotting, 255.
- Log-log plot, hardness test, load-diameter relationship, 662.**
- LONGYEAR, R. D. and DONOVAN, P. W.: *Core Drilling Technology: Diamond Drills*, xxiii.**
- Lost Soldier Oil Field* (KRAMPERT), xix.**
- Lost Soldier, oil and gas field, A. I. M. E. trip, xvii.**
- LUCAS, F. F.: on hardening of steel, 863, 866, 868, 872, 899.**
 on nature of martensite in carbon steel, 877.

- LUCAS, F. F.: *Introduction to Ultra-violet Metallography*, xxvi, 909, 924; Discussion, 924-925.
- Lumberton sands: stripping: problems, 382.
view, 383.
- M
- McADAM, D. J., JR.: *Endurance Properties of Non-ferrous Metals-I*, xx.
- McADAM, D. J., JR.: *Endurance Properties of Non-ferrous Metals-II*, xxv.
- McCANCE, A., on hardening of steel, 864, 866, 869, 870, 872, 900, 1145.
- Maclean Institute of Metals brasses, analyses, 800.
- McCLENAHAN, J. S.: *Discussion on Lead Antimony System of Hardening of Lead Alloys*, 539.
- McCORMACK, C. P.: *Discussions on: Classification in Witwatersrand Mills*, 249, 250.
Investigation of Crushing Phenomena, 311, 314.
- McDougall roasters: lead ore: description, 174.
operation, 174-177.
- McELROT, G. E.: *Some Important Factors in Metal-mine Ventilation*, xxiv.
- McGill University, crushing tetasts, 310.
- McGRAW, F. R.: *Corrosion of Pipe Lines and Protective Covering*, xxiii.
- MACVICHIE, DUNCAN: *Iron Fields of the Iron Springs and Pinto Districts, Iron County, Utah*, xviii.
- McWHIRT, BURN: *Kansas-Oklahoma (Petroleum Production)*, xxiv.
- MADGE, W. C.: *Discussion on Method of Unloading and Coarse-crushing Practice at Magna Plant, Utah Copper Co.*, 224.
- MADGE, W. C. and ALLEN H. P.: *Chloridizing Mill of the Standard Reduction Co.*, xix, 317-338.
Tintic Standard Co's. mill, xviii.
- Magna plant: coarse crushing: flow sheet, 216.
methods and machinery, 215, 218, 220.
section, 214.
construction, 219.
conveyors: description, 217, 220, 223.
speed, 217, 224.
view, 221.
cost data, 223.
dumping methods, description, 213-215.
equipment, views, 217-222.
ore, transportation, storage and handling, methods, 212, 213, 215-218, 220.
primary crushing, method, 213.
primary rolling, description, 222.
secondary crushing, method, 220.
screening towers, view, 222.
- Magnesia, in glass sands, occurrence and effect, 405.
- Magnesium, open-hearth slag, variation, 1083, 1089.
- Magnesium-aluminum alloys, aging rate, effect, 539.
- Magnesium oxide, crystal, atomic structure, data, 644.
- Magnesium spark, metallography, use, 916, 919-922.
- Magneton numbers, rare earths, 639, 640.
- Making Rimmed Steel (PARACM), xxvi, 1026; Discussion, 1036-1046.
- Manganese: open-hearth charge: decrease during run, curves, 1080, 1084.
effect, 1035, 1044-1045.
open-hearth process: elimination, reaction formula, 1113.
equilibrium: data, 1121.
reactions, 1114.
slag basicity, effect, 1120.
temperature effect: 1118.
curves, 1116, 1120.
open-hearth slag, variation, curves, 1083, 1086.
residual, calculation, 1122.
- Manganese alloys, aluminum base: see *Piston alloys*.
- Manganese bronzes: heat treatment, effect, curves, 1170.
structure, photomicrograph, 1169.
- Manganese-nickel bronzes, analysis, 800.
- Manganese ores, clay in, grinding troubles, 250.
- Manhattan schist, logarithmic size-curves, 301-303, 308, 309.
- MANN, H. T.: *Effect of Zinc Oxide on the Formation Temperatures of Some Ferroas Slags*, xxv, 3.
- MANNING, VAN. H.: *Research and the Oil Industry*, xxiii.
- Map, Kramer, Calif., 455.
- Mapleton Depot, Pa., glass, sand, shape of grains, view, 410.
- Marketing: see *Cement copper*.
- Martensite: carbide molecules, position, 869.
carbon atoms, position, 869, 896.
carbon in, condition, 862.
constitution, 1147.
development along cleavage planes, sketch, 878.
examples, photomicrographs, 1149, 1150.
formation, conditions, 867.
fresh, hardness, cause, 1146.
hardening of steel, effect, 860.
hardness, cause, 867, 874, 907, 1007, 1145.
heating, effect, 1146.
iron and carbon in, bond, 865.
iron in, condition, 861.
non-ferrous alloys, 1155.
structure, discussion, 877.
troostite in, photomicrograph, 946.
ultra-violet light: selective characteristics, 924.
photomicrographs, 919-921.
- MARVIN, THEO.: *Some Drilling and Blasting Methods for Mining Coal in the United States*, xxvii.
- Mascotte tunnel: see *Ohio Copper Co. mine*.
- Mass action, distribution, law, 1108.
- MATHEWS, J. A. on hardening of steel, 864, 866, 872, 900.
- MATHEWSON, C. H.: *Discussion on Action of Reducing Gases on Heated Copper*, 773-774.

- MATHEWSON, E. P.: *Discussion on Effect of Zinc Oxide on the Formation Temperature of Some Ferrous Slags*, 28.
- MATHEE, F.: *Ore Occurrences of the Park City District*, xviii.
- Matte: see *Lead blast-furnace matte*.
- Mechanical efficiency: see *Kick's law vs. Rittenger's*.
- Mechanical Properties of the Aluminum-copper-silicon Alloy as Sand Cast and as Heat-treated* (DANIELS and WARNER), xx, 464-478.
- Mechanism of Filtration* (HIXSON, WORK and ODELL), xxv, 225; Discussion, 234-238.
- MECHIN, R. J.: *Top Slicing in Old Fills at El Bordo Mine, Mexico*, xxvii.
- MEISSNER, K. L.: *The Microstructure of Aluminum*, xxv, 622-626.
- Melting tests, Seger cones, 12.
- Memphis, Tenn., lignite, removal from sand and gravel, 430.
- MERRIS, M. H.: *Improvements in the Series System of Electrolytic Copper Refining Recently Developed by the Nichols Copper Co.*, xxv, 123.
- Discussion on Improvements in the Series System of Electrolytic Copper Refining Recently Developed by the Nichols Copper Co.*, 142-144.
- Metallography: bibliography, 1175.
- blue light, photomicrograph, 922.
- committee, xiii.
- identification of structures, 924.
- non-metallics, 1173.
- research, review, 1135.
- shortcomings, 904.
- spark used, discussion, 916.
- ultra-violet: apochromatic system, comparison, 919.
- bas-relief, causes, 925.
- equipment: description, 910.
- diagram, 913.
- views, 911, 912.
- exact focusing, importance, 915.
- illuminating beam, restriction: 916.
- effect, 921.
- optical combinations, 917.
- optical system, diagram, 910.
- plates, 918.
- photomicrographs, 917-923.
- resolution obtainable, 919.
- selective absorption, 924.
- see also, *Monochromat objectives; Quartz eye-pieces; Photomicrographs*.
- Metalloids: basic open-hearth: elimination tests, charge, variation during run, curves: 1080.
- coal rate, 1097.
- conclusions, 1096.
- curves, 1084, 1085.
- description, 1079.
- ferromanganese used, analysis, 1105.
- ferrosilicon used, analysis, 1105.
- furnace temperatures, curves, 1092.
- metal during run, analyses, 1098.
- raw materials, analyses, 1105.
- Metalloids: basic open-hearth: elimination tests, charge, variation during run, curves: results, 1088.
- sampling methods, 1081.
- scrap used, analyses, 1105.
- slag: analyses during run, 1101.
- variation curves, 1082, 1083, 1086-1090.
- weights, 1091.
- sulfur in furnace, 1093.
- Metallurgical cyanide, flotation in British Columbia, 371.
- Metallurgical sand, properties and uses, 445.
- Metallurgy: relation of atomic structure, 628.
- see also *Institute of Metals; Iron and Steel; Non-ferrous metallurgy; Open hearth*.
- Metals: atomic structure, need for more data, 628, 653.
- grain-growth loss: 1138.
- photomicrographs, 1140.
- intercrystalline brittleness: discussion, 750.
- photomicrographs, 751-753.
- lattice structure, 647.
- structures, description, 1135.
- see also *Precious metals; Uncommon metals; and metals named*.
- Method of Unloading Ores and Coarse-crushing Practice at Magna Plant of Utah Copper Co. (MIX and BARKER)*, xviii, 212; Discussion, 224.
- Mexican Oil Fields* (GARFAS and WHEATSEL), xiv.
- Meyer's analysis: ball indentation test: annealed copper: chemical analyses, 665.
- hardness measurements, 666.
- photomicrographs, 660, 661.
- results, data, 667, 669.
- spectrographic analyses, 665.
- cold-rolled copper, results, 669.
- feature, 657.
- load-diameter relationship: discussion, 568-664, 671-675.
- equation, 659.
- log-log plot, 662.
- load, relation to bearing strength, curves, 672.
- loading time, effect, curve, 659.
- limitations, 677-678.
- Michigan: see *Sylvania sand*.
- Microscopic Structure of Copper (PULSIFER)*, xxvi, 707; Discussion, 739-741.
- Microscopical sizing, difference with screen sizing, correlation, 316.
- Microstructure of Aluminum (MEISSNER)*, xxv, 662; Discussion, 626-627.
- Midvale, Utah: A. I. M. E. trip, xvii.
- electrostatic mill: description and use, 248.
- dust-collecting system, 350.
- heads and products, analyses, 350.
- recoveries, 351.
- flotation mill, description and use, 351.
- milling problem, 342.
- ores treated, description, 342.
- plant, equipment, 173.
- tube mill feed and product, analyses, 346.
- wet mill: practice and equipment, 342-348.
- recoveries, 351.

- MILLER, A. E.: *Treating (Oil Refining Processes)*, xxiii.
- MILLER, M. B.: *Wax Separation*, xxiii.
- MILLER, R. S. and BARDWELL, E. S.: *Use of Pulverized Coal in Copper Refining Furnaces*, xviii.
- MILLER, WALTER: *Basic Changes in Refining Processes*, xxiii.
Economic Effect of Basic Changes in Refinery Operation, xxiii.
- MILLIKAN, C. V.: *Use of Gas Meters for Determination of Pay Strata in Oil Sands*, xix.
- Milling methods, committee, xii.
- Milling papers, lists, xviii, xxv.
- Milling Practice at Midvale (LEMKE), xix, 342-353.
- Mills: see *Ball mill*; *Hardings conical*; *Midvale*; *Rod mill*; *Standard Reduction Co. mill*.
- Millville, N. J., sands: hydraulic mining; 384.
view, 386.
mining and preparation: 384, 387.
views, 385.
mining costs, 384.
stripping problems, 382.
- Milwaukee, Wis., bentonite use, 389.
- Mine ventilation papers, xxiv.
- Mining: see *Sands*.
- Mining and Preparation of Eastern Molding Sands* (BIRD), xxv, 381; Discussion, 388-393.
- Mining geology papers, lists, xviii, xxvi.
- Mining laws, borate deposits, inaccuracies, 461.
- Mining Methods in Grass Valley District, Calif.* (FULTON and FOOTE), xxvii.
- Mining methods papers, lists, xviii, xxiv, xxvii.
- Mining Petroleum in France and Germany* (RICE and DAVIS), xxiv.
- Minnesota, industrial sands, occurrence, 434.
- MISER, H. D. and others: *Mississippi Valley Field (Petroleum Production)*, xxiv.
- Mississippi Valley Field (Petroleum Production)* (MOULTON, MISER and LOGAN), xxiv.
- Missouri: glass sand, occurrence and mining, 420.
industrial sands, occurrence, 434.
- MIX, B. E.: *Discussion on: Method of Unloading and Coarse-crushing Practice at Magna Plant, Utah Copper Co.*, 224.
- MIX, B. E. and BARKER, L. M.: *Method of Unloading and Coarse-crushing Practice at Magna Plant, Utah Copper Co.*, xviii, 212-223.
- MITAKE, M. and STOUTON, BRADLEY: *Preliminary Study of Magnesium-base Alloys*, xxv.
- Modification and Properties of Sand-cast Aluminum-Silicon Alloys* (ABCHER and KEMPF), xxv, 581; Discussion, 619-621.
- Moisture: see *Coke*; *Iron Ore*.
- Molding materials, brass, discussion, 832.
- Molding sands, eastern, mining and preparation, 381-388.
- Molds: see *Rimmed steel*.
- Molybdenite, sodium-cyanide flotation tests, 370.
- Molybdenum, effect on hardness of iron, 1006.
- Monochromat objectives; description, 914.
magnifications, 914.
optical camera-lengths, 914.
- Montana; see *Butte*.
- Moore filter: description, 163.
view, 159.
- MOORE, H. F.: *Notes on the Fatigue of Non-ferrous Metals*, xx.
- MOULTON, G. F. and others: *Mississippi Valley Field (Petroleum Production)*, xxiv.
- Mt. Holly: see *Lumberton sands*.
- Mt. Union Sand Flotation Plant for the Preparation of Bituminous Coal (T. M. CHANCE), xxvii.
- MUELLER, W. A. and others: *Treatment of the Telluride-bearing Gold Ores of the Wright-Hargreaves Mines, Ltd.*, xxv.
- Muffle furnace: see *Ferrous slags*, formation temperature tests.
- MULLIGAN, J. J., COLCORD, F. F., KERN, E. F. and: *The Conductivity of Electrolytes in the Electrolytic Separation of Gold and Silver*, xxv, 108-117.
- Multiple system: see *Electrolysis, copper*.
- Murray, Utah: A. I. M. E. trip, xvii.
Germania plant, practice, 172.
lead-smelter at, practice, 172.

N

- Natural gas, open-hearth fuel, controlled combustion, data, 1068-1071, 1074, 1075.
- Naval brass: heat treatment, effect, curves, 1171.
structure, photomicrographs, 1169.
- Naval Oil Reserves* (M. W. BALL), xix.
- Near East (Petroleum Production)* (PORCH), xxiv.
- Necrology, 1926, xxviii.
- NELSON, W. A.: *Discussion on Mining and Preparation of Eastern Molding Sands*, 388-389.
- Nernst's law of distribution, 1109.
- Neumann bands: alpha iron, characteristic, 966.
appearance, 964.
armor, photomicrographs, 1153.
discussion, 1139.
effect, determination, standard, 964.
effect on solubility of iron: curves, 963.
data, 956.
discussion, 955.
formation: effect of explosion air-gap: discussion, 948, 966.
photomicrographs, 950-954, 957-962.
further studies needed, 955.
photomicrographs, 957-962, 1140, 1153.
production by compression, 965.
twinning theory, discussion, 964.
- New By-product Coke Plant of the Columbia Steel Corporation* (KEIGLEY), xviii.
- New Cornelia Copper Co.: cathode, solubility in electrolyte, prevention, 79.
extraction data, different size ores, 76.
leaching: comparison 74-80.
depth of solution penetration, 77.
discard, 77.
unleached areas, causes, 78.
leaching plant, data, 106.

- New Cornelia Copper Co.:** lixiviant, content, 77.
ore, copper distribution in different sizes, 75.
solubility tests, chalcocite and chalcopyrite, 77.
tailings, copper distribution, 76.
- New Jersey:** glass sand, occurrence and mining, 420.
industrial sands: occurrence, 434.
photomicrographs, 440-444.
see also *Millville: Lumberton*.
- New York:** see *Albany sands; Laurel Hill*.
- New York meeting, 1926:** xxi.
technical sessions, xxii.
- New York Section, A. I. M. E., joint session,** xxii.
- Nichols Copper Co.:** charging cathodes, method, 138, 139.
electrolytic method; see *Electrolysis, copper*.
proposed plant improvements, 140.
wire-bar furnace: practice, 138-140.
equipment, views, 138-140.
- Nickel:** effect in: aluminum brass, data, 823.
nickel brasses: 802.
photomicrographs, 804, 805.
intercrystalline brittleness, photomicrograph, 752.
introduction in aluminum brass, method, 816.
- Nickel alloys, aluminum base:** see *Piston alloys*.
- Nickel and iron:** see *Aluminum brass*.
- Nickel and tin:** see *Aluminum brass*.
- Nickel brasses:** high-sinc, physical properties, 799.
physical tests, description, 801.
see also *Aluminum brass; Brass*.
- Nickel-iron:** see *Iron-nickel*.
- Nickel-manganese bronze, analysis,** 800.
- Nickel silver:** annealing: internal stress: quality, effect, curves, 836.
temperature effect: curves, 845, 846.
data, 843, 844.
annealing cracking, causes and prevention, 847.
changes during heating and cooling, 834.
cracking temperature, determination, 835.
cracks, types, photomicrographs, 839-841.
grain size: effect of annealing time: curves, 837.
data, 838.
tensional stress from change of curvature, formula, 843.
test specimens, analyses, 836, 842.
- Nip angle, crushed rock, relation to size of particle and ball, diagram,** 277.
- Nip theory:** see *Rod mills*.
- Nitric acid:** as etching reagent, 731, 735.
in electrolytes, effect, 120.
- Nitrogen blowholes in rimmed steel, discussion,** 1032, 1042, 1045.
- Nitrogen-iron:** see *Iron-nitrogen*.
- NIX, F. C.:** *Discussion on the Lead Antimony System of Hardening of Lead Alloys*, xxv, 529-535.
- NIX, F. C., ZICKERICK, LYALL, and DEAN, R. S.:** *The Lead Antimony System and Hardening of Lead Alloys*, xxv, 505-529.
- Nogales, Ariz., mill, sodium-cyanide flotation tests,** 370.
- Non-ferrous alloys:** martensitic structure, 1155.
structure, photomicrographs, 1158.
see also alloys named.
- Non-ferrous metallurgy:** committee, xii.
papers, lists, xviii, xxv.
- Non-metallic metallography,** 1173.
- Non-metallic minerals:** A. I. M. E. committee, xiii.
papers, list, xxv.
- North Carolina, filter sand, photomicrograph,** 439.
- Northport (Wash.) plant, lead smelting practice,** 198.
- Notes on the Fatigue of Non-ferrous Metals (MOORE),** xx.
- Notes on Geology of Tintic District (CRANE),** xviii.
- O
- Obituaries, deceased members,** xxxi.
- ODELL I. H., HIXON, A. W., WORK, L. T. and:** *Mechanism of Filtration*, xxv, 225-234.
- Officers, A. I. M. E., 1926-1927,** xi.
- Ogden Portland Cement Co., oxidized tailings test, results,** 203.
- Ohio Copper Co:** copper-concentrates: briquets: copper content, 51.
moisture content, 51.
physical properties, 51-53.
shapes tested, 52.
tests, description, 51-53.
briquetting: advantages, 51, 53.
pressures used, 51-53.
water in, 50.
- leaching old workings:** barren solutions, copper content, 48.
conclusions, 42.
copper: production, 31, 33.
recoverable, 55.
film-water percolation, advantages, 39-42.
financing, means, 31, 32.
General Manager's report, 32.
iron: harmful effect: 36.
overcoming, 44.
mass percolation, advantages and disadvantages, 38-42.
methods and principles, 31-57.
operating costs, 53, 57.
pregnant solutions: analyses, 47.
copper content: 41-42, 48
solubility in water, 42.
recovery: 1924, 48.
statistics, 32.
scrap iron used, 33.
smelting charges, 53.
water: analyses, 43.
supply, 42-43.
volume, 47.
water and air, factors in applying, 34.
- mine:** caved zone: survey of, 54.
tonnage in, 54-55.
chalcocite, presence, 34.
Dederich tunnel: purpose, 38.
use, 54.
work in, 41.

- Ohio Copper Co.: leaching old workings: Mine:
 Mascotte tunnel: leaching equipment,
 47.
 use, 33.
 orebody: caving for leaching, possibility,
 54, 55.
 leached, description, 33-34.
 permeability to water, 33.
 precipitation: iron consumption, 50, 56.
 method, description, 46-50.
 plant, description, 46.
- Ohio, industrial sands, occurrence, 434.
- Oils: as power fuel, 98.
 flotation, 353.
 see also *Crude oil; Petroleum*.
- OLDRIGHT, G. L.: *Discussion on Production of Ferric Sulfate and Sulfuric Acid from Roaster Gas*, xix, 103.
- Olivite pump, description and use, 337.
- OLMSTED, S. G.: *Discussion on Chief Consolidated Volatilisation Process and Mill*, 210.
- O'NEILL, F. W. and VAN FLEET, H. V.: *Liquid Oxygen as an Explosive*, xxvii.
- Ontario mine, A. I. M. E. trip, xvii.
- Open-hearth committee, xiii.
- Open-hearth furnace, basic: available heat in bath, 1071-1073.
 charge, furnace and ladle additions, efficiency, 1096.
 combustion: automatic control: conclusions, 1063.
 data: 1068-1078.
 discussion, 1050.
 operating results, 1058.
 calculations: 1047.
 discussion, 1050.
 control: equipment: description, 1055.
 figures, 1064-1067.
 combustion air, weight, 1068.
 combustion products, weight and heat content, 1068, 1069.
 combustion regulators, sections, 1066, 1067.
 equilibrium, false, 1113.
 fuel: flow, rate, 1075.
 latent heat, 1074.
 supply, continuous, importance, 1062.
 gas-fired, layout, 1065.
 lining erosion: data, 1094.
 factors, 1093.
 preheating air and fuel, heat available, 1070.
 production and consumption: producer-gas fired, 1060, 1061, 1076.
 coke-oven gas and tar fired, 1060, 1061, 1077.
 rebuilding costs, 1062.
 see also *Rimmed steel; Slag*.
- Open-hearth papers, list, xxvi.
- Open-hearth process, basic: dead heat and good bath, comparison, 1110.
 elimination reactions, 1109.
 equilibrium tests: data, 1098 1132.
 laboratory, 1114.
 metal and slag, analyses, 1098, 1132.
 results: carbon, 1122.
 manganese, 1115.
 phosphorus 1125.
- Open-hearth process, basic: lime boil, equilibrium, 1117.
 see also *Metalloids; Slag*.
- Optical combinations, ultra-violet metallography, 917.
- Ore Deposits and Their Relation to Structural Geology* (BREMSON), xviii.
- Ore Occurrences of the Park City District* (MATHEW), xviii.
- Ores: transportation, storage and handling, methods, 212-223.
 unloading, see also *Magna plant*.
- Ore sizes, leaching tests, 61-63.
- Organic matter, in glass sands, occurrence and effect, 406.
- Organisation of Industry* (ROBERTS), xxvii.
- Oriakany sands, grades, 419.
- Operating Characteristics of Centrifugal Fans and Use of Fan Performance Curve* (HUBER), xxiv.
- OSBORN, C. C. and SNADS, J. M.: *Forecasting Petroleum Production*, xxiv.
- OSMOND, F., steel hardening theory, 1145.
- OSTRANDER, F. T.: *Argentine (Petroleum Production)*, xxiv.
- Ottawa, Ill.: filter sand, photomicrograph, 438.
 sand-blast sand, photomicrograph, 441.
 sandstone, glass sand from, photomicrograph, 411.
- Oxide volatilisation, conditions for, discussion, 210.
- Oxychloride cement-plaster sand, properties and uses, 445.
- Oxygen: in air, weight, 1011.
 in copper, effect, 682.
 in film water, 39.
 in refined copper: direct determination: apparatus: description, 785, 792.
 sketches, 792, 793.
 views, 785, 786.
 method, description, 788, 793.
 sample, preparation, 787, 790.
 indirect determination, description, 795.
 relation to heating temperature: curves, 788.
 data, 789.
- Oxygen consumption: see *Blast furnace*.
- Oxygen content, air, 1011.
- Oxygen eutectic: see *Copper, microscopic structure*.
- Oxygen-free copper versus "tough-pitch" copper, use, 742.

- Pachuca tanks, comparison with Greenawalt apparatus, 103.
- Pacific Coast Borax Co., control of borax lands, 453.
- Pacs flux, aluminum-silicon alloys, action, 581.
- Painting, cathodes, process, 128.
- Paraffin: as bond, Seger cones, 7.
 impregnation of cathode, 120.
 trip, xvii.
- Park City, Utah, A. I. M. E. trip, xvii.
- Park City Mining & Smelting mines, A. I. M. E.
- Park-Utah mines, A. I. M. E. trip, xvii.

- PARMELEE, C. L.:** *Factors Affecting the Cracking of Petroleum*, xxiii.
- PARR, S. W.:** *Relation of Origin and State of Carbonisation of Coal to Problems of Low-temperature Carbonization*, xxvii.
- PARSONS, A. B.:** *Discussions on: Classification in Witwatersrand Mills*, 251.
Mechanism of Filtration, 237.
- Pearlite:** hardness, causes, 1145.
structure, sketch, 874.
transformation of austenite to, diagrams, 880.
ultra-violet selective characteristics, 924.
- Pebble mill:** wear tests: 266.
without pebbles, 264.
- PEIRCE, CARL:** *Making Rimmed Steel*, xxvi, 1026-1036.
- Pennsylvania:** glass sands, occurrence, mining, and preparation, 414.
industrial sands, occurrence, 434.
see also *Mapleton Depot; Pottsville*.
- Percolation leaching**, description, 319.
- Permissible Limits of Toxic and Noxious Gases in Mine and Tunnel Ventilation (SAYERS)**, xxiv.
- PERROTT, G. ST. J.:** *Discussion on Effect on Air Gap in Explosion System on Production of Neumann Bands*, 966.
- PETERS, W. A., JR.:** *Fractionation*, xxiii.
Petroleum mining methods, papers, xix.
Petroleum papers, lists, xix, xxii-xxiv.
Petroleum Statistics and the Economic Situation (KNAPP), xxiv.
- Phosphor bronze**, heat treatment, 1172.
- Phosphorus:** effect on open-hearth equilibrium, 1120.
equilibrium tests, charge, analyses, 1129.
open-hearth charge, decrease during run, curves, 1080, 1085.
open-hearth process: elimination: laboratory data, 1126.
plant data, 1127, 1129.
reactions, 1125.
residual, calculation, 1129.
temperature effect, curve, 1128.
open-hearth slag, variation, curves, 1083, 1087.
- Photoelectric phenomenon**, metal crystals, discussion, 651.
- Photomicrographs:** aluminum alloys, 1158.
aluminum-base piston alloys, 499-503.
aluminum-copper alloys, 565-566, 569-600, 572-573, 575, 576.
aluminum silicon alloys, 473-475, 582-584, 603-613.
annealed copper bars, 660, 661.
armor, structure, 1153.
ball-mill products, 279, 282.
banded ferrite, 945.
blue light, 922.
brasses: effect of: aluminum, 808.
aluminum-nickel-tin, 827, 828.
iron, 813-815.
nickel, 804, 805.
bronzes, 1169.
burst boiler tube, 1145, 1152.
- Photomicrographs:** carbon steel, furnace and air-cooled, 934-939, 941-944.
copper: deoxidation, depth, 765.
effect of reducing gases, 747.
lead and tin-bearing, 684-687, 690, 691.
copper-aluminum diffusion alloys, 1156.
copper casting exudations, 701-705.
copper-cuprous oxide, with and without annealing, 777-781.
crushed rock, number and size of grains, 304-306.
effect of cyanide solution: galena, 365, 367.
pyrite, 366, 369, 377-379.
sphalerite, 366, 388.
glass sands, 410-412.
grain-growth loss, metals, 1140.
gun metal, 1169.
industrial sands, 438-444.
intercrystalline brittleness in metals, 751-753.
iron-tungsten alloys: 972-983.
grain size, tungsten-content, effect, 986.
iron-tungsten-carbon alloys, 1004, 1005.
martensite, examples, 1149, 1150.
Naval brass, 1169.
Neumann bands: explosion air-gap tests, 950-954, 957-962.
armor, 1153.
nickel silver, cracks, types, 839-841.
non-ferrous alloys, 1158.
preparation of specimens, 731-739, 741.
quartz: rod-mill products, 269.
roll-crushed, 261.
wear-test products, 266.
silver crystals formed in electrolysis, 115-116.
steel, hardened, 875, 876, 877, 879.
troostite: examples, 1149, 1150.
in martensite, 946.
ultra-violet metallography, 917-923.
- Photomicrography:** see *Metallography*.
- Physical-chemical laws:** see *Mass action; Nernst's law; Van't Hoff isochore*.
- Physics**, iron and steel, committee, xiii.
- Pig iron:** see *Rimmed steel, charge*.
- PILLING, N. B.:** on action of reducing gases on copper, 745.
Discussions on: Action of Reducing Gases on Heated Copper, 772-773.
Effect of Lead and Tin with Oxygen on the Conductivity and Ductility of Copper, 695, 697-699.
- PILLING, NO. B. and HALESWELL, G. P.:** Effect of Lead and Tin with Oxygen on the Conductivity and Ductility of Copper, xxvi, 679-692.
- Pilot plant:** definition, 99.
see also *Inspiration Cons. Copper Co.*
- Piston alloys:** aluminum base: before and after tests; photomicrographs, 499-503.
physical properties, 482, 483.
etching, method and reagents, 485.
heat-treatment, description, 483.
ingots, chemical composition, 481.
raw materials, chemical composition, 481.
reheating tests: conclusions, 497.
procedure, 483.

- Piston alloys: aluminum base: reheating tests: purpose, 481.
results: data, 486-487.
curves, 490, 492-495, 497.
discussion, 489-497.
test bars: mechanical tests, description, 484.
mold: view, 482.
preparation, 483.
unetched, colors and characteristics, 485.
Plastic fire, physical properties, 392.
POGUE, J. E.: *Relation between Price and Stocks of Gasoline*, xxiv.
Trend of Prices in the Petroleum Industry, xxiv.
PORCH, E. L., JR.: *Near East (Petroleum Production)*, xxiv.
PORTER, J. B.: *Discussions on: Investigation of Crushing Phenomena*, 310.
Mechanism of Filtration, 235.
PORTEVIN, A.: on hardening of steel, 865, 868, 887.
Portland filters, view of, 204.
Possibilities of Future Production from the Pro-Chattanooga Series of Northeastern Oklahoma (WHITE), xxiv.
Potassium bromide crystal, lattice energy, compressibility, and pressure coefficient, 646.
Potassium chloride crystal: lattice energy, compressibility and pressure coefficient, 646.
lattice structure, data, 644.
Potassium fluoride crystal, lattice energy, compressibility and pressure coefficient, 646.
Potassium iodide crystal, lattice energy, compressibility and pressure coefficient, 646.
Potassium nitrate, electrolytes, effect on conductivity, 120.
Potomac River sand, photomicrograph, 440.
Potter's sand, properties and uses, 443.
Pottsville, Penn., sandstone, glass sands from, 419.
Pouring, brass molding, discussion, 833.
Pouring dishes, melted brass, discussion, 833.
Power consumption, electrolytic copper refining, 131.
Power supply: see *Standard Reduction Co. mill*.
Precious metals, extraction and refining, committee, xii.
Precipitation: copper, cost, 104, 105.
see also *Electrolytic precipitation*; *Iron*; *Ohio Copper Co.*; *Sulfur dioxide*.
Precipitation plant: see *Ohio Copper Co.*
Precipitation rate: see *Copper, leaching*.
Precipitation theory, aluminum-copper alloys, 577.
Precipitators, description, 334, 336.
Preliminary Study of Magnesium-Base Alloys (STOUGHTON and MITCHELL), xiv, 541; Discussion, 557-559.
Premier mine, B. C., flotation by metallurgical cyanide, 371.
Preparation and Uses of Special Industrial Sands (WEIGEL), xxv, 434; Discussion, 448.
Prerostasting, lead ore, Utah practice, 174.
Pressure versus vacuum filter, discussion, 235.
Pressures, high, filtration, effect, 235.
PRICE, W. B.: *Discussions on Annealing Cracking of the Nickel Silvers*, 849.
Lead Antimony System of Hardening of Lead Alloys, 535.
PRIMROSE, J. A.: *Distillation by Pipe Stills*, xxiii.
Probable Error in Blast-furnace Records and Calculations Therefrom (READ), 1009; Discussion, 1023-1025.
Problems of Pumping Deep Wells (UREN), xix.
Producer gas, open-hearth fuel, controlled combustion, data, 1068-1077.
Production: see *Bingham mines, Utah*; *Zinc*.
Production of Ferric Sulfate and Sulfuric Acid from Roaster Gas (OLDBRIGHT, KEYES and WARTMAN), xix, 84; Discussion, 98-107.
Pulp: see *Filtration*.
PULSIFER, H. B.: *Microscopical Structure of Copper*, xxvi, 707-739.
Discussion on Microscopic Structure of Copper, 740, 741.
Pulverising, white lead for shipment, 166.
Pulverising sand, properties and uses, 445.
Pump: see *Olivite pump*.
PYNE, F. R.: *Discussion on: The Conductivity of Electrolytes Used in the Electrolytic Separation of Gold and Silver*, 120.
Effect of Lead and Tin with Oxygen on the Conductivity and Ductility of Copper, 695.
Exudations on Copper Castings, 706.
Improvements in the Series System of Electrolytic Copper Refining as Recently Developed by the Nichols Copper Co., 144.
Lead Antimony System of Hardening of Lead Alloys, 538.
Pyrite: gold-bearing, recovery, 342.
see also *Cyanide solutions, flotation tests*.
Pyro- and Hydro-treatment of Magnesite and Dolomite (HENTON), xxv.
Pyrometer; radiation-protected; arrangement, diagram, 1064.
use, 1047.

Q

- Quantum theory, atomic structure, explanation, 630.
Quarrying, glass sands, practice, 415.
Quartz: ball-mill product: photomicrographs, 279.
screen analyses, logarithmic plots, 274-277, 280, 281, 283-286.
rod-mill products: photomicrographs, 269.
screen analyses, logarithmic plots, 270, 271, 273.
roll-crushed: photomicrographs, 261.
screen analyses, logarithmic plots, 256, 257, 259.

- Quartz: wear tests: conclusions, 266.
curves, 267.
data, 266.
sand, wear tests, description and results, 264-268.
- Quartz eye-pieces: description, 914.
magnifications, 914.
optical camera-lengths, 914.
- Quartzite: for glass sand, disadvantages, 422.
occurrence and use, 422.
- Quenching temperature, effect on impact values, 937.
- Questionnaire: see *Steel, hardening, theories*.
- R
- RADER, C. M. and ARMSTRONG, R. O.: *Water Shut-off Methods in Salt Creek Field*, xix.
- RADER, C. M. and ESTABROOK, E. L.: *History of Production of Salt Creek Field*, xix.
- Radiation: see *Pyrometer, radiation-protected*.
- Rail bonds, embrittlement, causes, 746.
- RALSTON, O. C.: *Discussion on The Chief Consolidated Volatilisation Process and Mill*, 210.
- RAMSEY, J. P., lead-antimony-tin alloys, hardening tests, 536.
- RANNEY, LEO: *Ranney Process of Mining Oil*, xxiv.
Ranney Process of Mining Oil (RANNEY), xxiv.
- Rare earths, magneton numbers, 639, 640.
- Raritan Copper Works: oxygen and sulfur determination, apparatus, view, 786.
use of Walker method, 124.
- RAWDON, H. S.: *Discussion on Embrittlement of Copper by Hot Reducing Gases*, 750-754.
- Rawlins, Wyo., A. I. M. E. trip, xvii.
- READ, T. T.: *Probable Error in Blast-furnace Records and Calculations Therefrom*, 1009-1023.
Discussion on Probable Error in Blast-furnace Records and Calculations Therefrom, 1023, 1025.
- Reagents: cyanide flotation: patent, 354
sulfides, 362.
flotation, 353.
piston alloys, aluminum base, etching, 485.
see also *Etching*.
- Recovery: see *Copper*.
- Recovery of Copper by Leaching, Ohio Copper Co. of Utah (ANDERSON and CAMERON)*, xviii, 31; *Discussion*, 55-57.
- Reducing gases: see *Copper, embrittlement; Copper deoxidation, Illuminating gas*.
- Redwood, for aerator tank construction, 95.
- REINHARTS, L. F.: *Discussion on Making Rimmed Steel*, 1036-1042, 1043, 1044, 1046.
- Relation between Metallurgy and Atomic Structure (FOOTE)*, xxv, 628-656.
- Relation between Price and Stocks of Gasoline (POGUE)*, xxiv.
- Relation of Ash Composition to the Uses of Coal (FIELDNER and SELVIG)*, xxvii.
- Relation of Origin and State of Carbonisation of Coal to Problems of Low-temperature Carbonisation (PARR)*, xxvii.
- REMMERS, W. E., CLAYTON, C. Y. and FOLEY, F. B.: *Influence of Temperature, Time and Rate of Cooling on Physical Properties of Carbon Steel-II*, xxvi, 927-947.
- Report of Coal and Coke Committee (EAVENSON)*, xxvii.
- Report of Sub-committee on Coal-mine Ventilation (HAAS)*, xxiv.
- Report of Sub-committee on Coal Mining to Committee on Ground Movement and Subsidence (EAVENSON)*, xxvii.
- Research and Oil Industry (MANNING)*, xxiii.
- Resinous paint, for cathodes, 128.
- Reverse-nozzle dust-collector, description and use, 91.
- Review of American (Petroleum) Production (FOHS)*, xxiii.
- REYNOLDERS, J. V. W.: *Discussion on Making Rimmed Steel*, 1043, 1046.
- RICE, G. S. and DAVIS, J. A.: *Mining Petroleum in France and Germany*, xxiv.
- RICHARDS, R. H.: *Discussion on Investigation of Crushing Phenomena*, 316.
- RICHARDSON, A. S.: *Economic Design of Mine Airways*, xxiv.
Theoretical Rating Compared with Operating Performance of Centrifugal Mine-Ventilating Fans, xxiv.
- RICHARDSON, H. H. and DIX, E. H.: *Equilibrium Relations in Aluminum-copper Alloys of High Purity*, xxv.
- RICKETTS, L. D.: *Discussions on: Leaching Mixed Copper Ores with Ferric Sulfate, Inspiration Copper Co.*, 82.
Mining and Preparation of Eastern Molding Sands, 389-390.
Preparation and Use of Industrial Special Sands, 448.
Standard Tests of Molding Sands, 397.
- RIES, H.: *Use of Standard Tests of Molding Sands*, xxv, 394-397.
- RING, D. T.: *Arkansas and Louisiana (Petroleum Production)*, xxiv.
- Rimmed steel: ammonia in, discussion, 1032, 1036, 1042, 1045.
- blowholes: formation: permissible, 1035, 1045, types and causes, 1032, 1039, 1042, 1045, 1046.
views, 1032-1034, 1040.
welding up, 1041.
- carbon in bath, amount, 1035, 1044-1045.
casting temperature, discussion, 1030.
charge: content, 1026, 1037.
pig iron, amount advisable, 1027, 1038.
definition, 1026.
deoxidiser, use, 1035, 1041.
manganese in bath, amount, 1035, 1044-1045.
manufacture: shaping the slag, discussion, 1030.
methods, 1026, 1036.
summary, 1036.
melting practice, discussion, 1028, 1037.
molds, condition, importance, 1038.
pouring practice, discussion, 1031.

- Rimmed steel: silicon in bath, effect, 1035.
theory, 1035.
- Rittinger's law of mechanical efficiency, versus Klok's, 298.
- Rivet: see *Boiler rivet*; *Deck rivet*.
- Roaster, making SO_2 , description, 90.
see *Roasting furnaces*.
- Roaster gas: oxygen and SO_2 content, 87.
dust-collecting, 88.
see also *Ferric sulfate and sulfuric acid, from roaster gas*.
- Roasting: see *Lead smelting*; *Standard Reduction Co. mill*.
- Roasting costs, discussion, 341.
- Roasting furnaces: description, 174.
flue dust and fume, retreatment, methods, 190.
- Robert W. Hunt medal, presentation, 1926, xxii.
- ROBERTS, G. E.: *Organization of Industry*, xxvii.
- ROBERTS-AUSTEN, steel hardening theory, 1145.
- Rock drill, broken, structure, photomicrographs, 1150.
- Rocks: see *Homogenous rocks*; *Heterogenous rocks*.
- Rockwell test, possible error, 657, 676-677.
- Rockwood, Mich.: see *Sylvania sand*.
- Rocky Mountain District (Petroleum Production) (Wood)*, xxiv.
- Rod mills: angle of nip theory, discussion, 315.
-200-mesh material, computed and observed, data, 288.
number of rods used, effect, tests, 272.
particle breakage, manner, 273.
rotation of rolls, diagram, 273.
see also *Homogenous rocks*.
sizing action, 255.
- Rolling plant: see *Magna plant*.
- Rolls: -200-mesh material, computed and observed, comparison, data, 288.
see also, *Braun pulveriser, rod and ball mill jaw crushers*; *Homogenous rocks, roll products*.
- Roofing sand, properties and uses, 445.
- ROSE, H. J.: *Selection of Coals for the Manufacture of Coke*, xxvii.
- ROSENHAIN and McMURHAN, work on Neumann bands, 964.
- Rubidium bromide crystal, lattice energy, compressibility and pressure coefficient, 646.
- Rubidium iodide crystal, lattice energy, compressibility and pressure coefficient, 646.
- Ruggles-Coles dryer, view of, 204.
- Russia, South, manganese ores, clay in, 250.
- Russia (Petroleum Production) (Zavoico)*, xxiv.
- S
- SACKETT, B. L.: *Discussion on Lead Smelting in Utah*, xviii, 197, 199.
- SACKETT, B. L., BARDWELL, CARLOS, JACOBSON, SIMON, and JENSEN, N. H.: *Lead Smelting in Utah*, xviii, 171-197.
- St. Peter sandstone, glass sand, photomicrograph, 411.
- Salida, Colo. lead-smelting practice, 198.
- Salt: in volatilisation charge: easily sintered ores, 211.
- Salt: in volatilisation charge: elimination, 201 209.
see also *Calcium chloride*; *Sodium chloride*.
- Salt creek oil field A. I. M. E. trip, xvii.
symposium papers, xiz.
- Salt Lake City: see *Standard Reduction Co. mill*.
- Salt Lake City meeting, 1925: xvii.
technical sessions, xviii.
- Salt Lake Iron & Steel Co., briquetting tests, copper concentrates, 51-53.
- Sand-blast sand: photomicrographs, 441-443.
properties and uses, 439.
- Sand casting, effect: see *Aluminum-copper-silicon alloy*.
- Sand-clay cores, physical properties, 392.
- Sand filtration, removal of iron from copper-leaching waters, 44.
- Sand: classification methods, 432.
foundry, see *Albany sands*; *Lumberton sands*; *Millville sands*.
impurities, removal, 424, 430-431.
mining costs, 384.
natural, grain shapes, 265.
river-bottom, mining, 384.
sharp and strong, definitions, 388.
shipments, quarantine restrictions, 382.
sizing, methods, 431-433.
synthetic mixtures, discussion, 390-391.
washing: methods, 426-431.
uniform feed, importance, 429.
water, amount, 428.
see also *Furnace-bottom sand*; *Industrial sands*; *Molding sands*.
- SANDS, J. M. and OSBORN, C. C.: *Forecasting Petroleum Production*, xxiv.
- SAUVEUR, A.: *Current Theories of Hardening of Steel Thirty Years Later*, 859; *Discussion*, 902-908.
- SAVAGE, H. J.: *Use of Pulverized Fuel*, xviii.
- SAYERS, R. R.: *Permissible Limits of Toxic and Noxious Gases in Mine and Tunnel Ventilation*, xxiv.
- SCHALLER, W. T.: on formation of coelemanite in place, 449.
- SCHERMERHORN, T. R.: *Discussion on: Hardness of Copper and Meyer's Analysis*, 674-675.
- SCHERMERHORN, T. R. and HOYT, SAMUEL L.: *Hardness of Copper and Meyer's Analysis*, xxvi, 657-671.
- Scrap: open-hearth, melting data, 1090.
see also *Brass melting*.
- Screen analyses: see *Heterogenous rocks*; *Homogenous rocks*.
- Screen sizing, microscopical, difference, correlation, 316.
- Screening: glass sands, methods, 416.
industrial sands, 437.
- Screening towers, Magna plant, view, 222.
- Screens, sand and gravel, 431.
- Searles Lake, Calif., borate deposits, 454.
- Seger cones: formation-temperatures, tests: bond, 7.
materials, 7.
mounting for firing, 9.
removal from mold, protection, 8.
melting tests, 12.

- Selection of Coals for the Manufacture of Coke* (ROSE), xxvii.
- Selenium, doré, removal, 122.
- SELVIG, W. A. and FIELDNER, A. C.: *Relation of Ash Composition to the Uses of Coal*, xxvii.
- Semilogarithmic curves, crushing tests, method of plotting, 255.
- Shale, removal from sand and gravel, 431.
- Sharpening and Handling Drill Steels at Franklin* (HAIGHT), xxvii.
- SHAW, EDMUND: *Washing and Sizing Sand and Gravel*, xxv, 424-433.
- SHAW, H. A.: *Discussion on Exudations on Copper Castings*, 706.
- SHAW, J. M.: *Employe Ownership in Industry*, xxvii.
- Shear tests: see *Aluminum-copper-silicon alloys*.
- Shovel Operations at Bingham Utah Copper Co.* (GOODRICH), xviii.
- Shunts: see *Contacts*.
- Shutting in Rangely Gas Well* (HOLMES), xix.
- Sieving: efficiency, discussion, 310-311. tests, results, 310.
- Silica: content in ferrous slags tested, 19-27. iron ore, variation, 1021. replacement by zinc oxide, slag-formation temperatures, 13-14, 17.
- Silica cores, physical properties, 392.
- Silicon: function as alloy, 464. modified alloys, effect, 601. open-hearth: bath, effect, 1035. charge, decrease during run, curve, 1080. slag, variation, 1082, 1087.
- Silicon alloys: see *Aluminum-copper-silicon alloy*; *Aluminum-iron-silicon alloys*.
- Silicon-aluminum alloys: see *Aluminum-silicon alloys*.
- Silver: concentrating recoveries, 351. leaching: effect of copper sulfate, curves, 324. free acid, need for, 324. sulfate content, control, 327. sulfates in solution: effect, curves, 325. data, 326. loss, Nichols series process, 133, 142, 144. precipitation: see *Standard Reduction Co. mill*. precipitators, Standard Reduction Co. mill, 336. volatilization, 210. recovery, 209.
- Silver alloys: see *Nickel silver*.
- Silver and gold separation: see *Electrolytes*.
- Silver content: see *Electrolytes*.
- Silver crystals: electrolytic separation: effect of ammonium nitrate on: 113-117. photomicrographs, 115-116. ion-electron lattice, 649, 650.
- Silver King Coalition mines, A. I. M. E. trip, xvii.
- Silver minerals, flotation in water, tests, 370.
- Silver nitrate solutions: conductivity: 108. curves showing, 109, 110. reactions, equations, 110.
- Silver precipitates, impurities, removal, 321.
- Silver-bearing galena, recovery, 342.
- SINCLAIR, E. G.: *Drilling Wildcat Wells in Wyoming*, xix.
- SINGSTAD, OLE: *Holland Tunnel*, xxiv.
- Sinter gases, SO₂ in, neutralisation, 181.
- Sintering: fines, treatment, methods, 180, 181. lead ore: sulfur problems, 180, 181. Utah practice, 177-182. pallet speed, 181.
- Sintering machine: see *Dwight-Lloyd*.
- Siphon lead well, invention, 172.
- Size curves: see *Homogenous rock*; *Logarithmic size-curves*.
- Sizing: microscopical and screen, difference, correlation, 316. rock crushing, importance, 311. see also *Gravel*; *Sand*.
- Sizing actions, crushing, description, 255.
- Sketch of Geology and Formations of Central Wyoming* (BARTHAM), xix.
- SKOWRONSKI, S.: *Discussions on: Action of Reducing Gases on Heated Copper*, 772, 773, 774. *Conductivity of Electrolytes Used in the Electrolytic Separation of Gold and Silver*, 120, 122. *Effect of Lead and Tin with Oxygen on the Conductivity and Ductility of Copper*, 692-694. *Improvements in the Series System of Electrolytic Copper Refining as Recently Developed by the Nichols Copper Co.*, 144.
- Slag: basicity, effect on manganese equilibrium, 1120. Burmo high-zinc, content and behavior, 28. equilibrium tests, composition, 1115, 1126. ferrit as zinc-carrying ingredient, 29. open-hearth: basicity: data, 1112. discussion, 1111. effect, 1119. index, 1111. composition during run, curves, 1082, 1083, 1086-1090. furnace tests: analyses during run, 1101. weights, 1091. iron-oxide formation, 1109. phosphorus content, effect, 1120. tapping and ladle: comparison: 1095. weights, 1090. see also *Ferrous slags*; *Lead blast-furnace, slag*.
- Slimes, fine, effect in mass of feed, 313.
- Slip interference theory: 1138. aluminum-copper alloys, 578. basis, 903.
- SMALLEY, OLIVER: *Special Nickel Brasses*, xx, 799-833.
- Smelting: see *Lead*.
- SMITH, A. W., lead-antimony alloys, conductivity curve, 512.
- SMITH, C. S.: *Discussion on Action of Reducing Gases on Heated Copper*, 770-771.
- SMITH, P. S.: *Alaska*, (Petroleum Production), xxiv.
- SMITH, W. C.: *Discussions on: Action of Reducing Gases on Heated Copper*, 773. *Effect of Lead and Tin with Oxygen on the Conductivity and Ductility of Copper*, 696.

- Soap bubbles, formation, analogy to crystal formation, 858.
- Soda ash: see *Sodium carbonate*.
- Sodium: modification of alloys: addition, method, 589.
amount needed, 588, 615.
loss on standing: curve, 594.
data, 596.
discussion, 590.
- Sodium bromide crystal: atomic structure, sketch, 643.
electron orbits, sketch, 644.
lattice energy, compressibility and pressure coefficient, 646.
- Sodium carbonate and lime, flotation of sulfides, effect, 356, 357, 359.
- Sodium chloride, for roasting, source, 322.
- Sodium chloride crystal, lattice energy, compressibility and pressure coefficient, 646.
- Sodium cyanide: chalcocypite and molybdenite, flotation, 370.
sulfides flotation, effect, 357.
- Sodium fluoride, crystal, lattice structure, data, 644.
- Sodium sulfate, as solvent for lead, 326.
- Soldering irons, embrittlement, causes, 746.
- Solidus curve, aluminum-copper alloys, discussion, 568.
- Solubility, sulfur dioxide in water, 88.
- Solutions, law of distribution in two solvents, 1109.
- Solvent agent: copper ores, content, 77.
see also *Ferric sulfate*.
- Solventicide: definition, 80.
importance, 81.
leaching, discard, 77.
use of term, 80-81.
see also *Antacid*.
- Some Drilling and Blasting Methods for Mining Coal in the United States* (MARVIN), xxvii.
- Some Economic Aspects of the Community Oil Lease* (WRIGHT), xxiv.
- Some Important Factors in Metal-mine Ventilation* (McELROY), xxiv.
- Sorbite: hardness, cause, 1145.
ultra-violet light: photomicrograph, 923.
selective characteristics, 924.
- South Dakota: see *Belle Fourché*.
- Spacing of Oil Wells* (BREWSTER), xxiii.
- SPARROW, S. W.: *Anti-knock Gasolines and Special Engine Development*, xxiii.
- Special Nickel Brasses* (SMALLEY), xx, 799-833.
- Specific gravity: see *Aluminum-copper-silicon alloy*; *Electrolytes, gold and silver separation*.
- Specifications: see *Aluminum-silicon alloys*; *Glass sands*.
- SPERRY, E. A., process for making white lead, 146.
- Sperry process: anode: molding and pressing, 150.
view, 153.
washing method, 167.
carbonating system, 162.
cathode: construction: 156-160.
plan, 158.
view, 156.
- Sperry process: cell construction, 152-156.
views, 152-156.
circulation of solutions, 160.
dryer, 164.
electrolytes for, 147.
electrolytic white lead, description, 146-148
Moore filter: description, 163.
view, 159.
plant: construction, 148.
equipment: 149, 168.
electrical, 167.
flow sheet, 164.
operating data, 168.
views, 150-156, 159.
product: barreling, 166.
characteristics, 168-170.
production and recovery, 166-167.
pulverizing, 16.
- Sphalerite: impurities, milling difficulties, 350.
see also *Cyanide solution*.
- Sponge copper, precipitation of silver, 320.
- Sponge iron, as precipitant, advantages, 339.
- Spring tensions, discussion, 312.
- Springa Mines, Ltd.: classifier speed, tests, 247.
mill tests, bowl versus cone classification, results, 248.
- Stamp mills: crushing action, 312.
sizing actions, 255.
- Standard Reduction Co.: mill: air lifts, description, 336.
crushers used, 331.
crushing, degree, 331.
fan, description, 334.
leaching: cycle, 319.
description, 323-327.
interfering elements, 325.
sulfate content, control, 327.
leaching solutions, heating system, 337.
leaching tanks, description, 334.
lead precipitated, part analysis, 320.
location, 317.
power supply, 338.
precipitation, description, 320, 321, 327.
precipitators, description, 336.
recoveries, 321.
roaster, description, plan and views, 332-335.
roasting: methods, 322.
preparation of ore, 318.
treatment costs, 321.
water supply, 338.
- ore, assay, 317.
- plant: description, 329.
plans and sections, 328-331.
treatment costs, discussion, 340.
- Standard sand, properties and uses, 445.
- Steel: carbon: see *Carbon steel*.
constituents, nature, 1146.
constitution, phase rule, discussion, 876, 903, 907.
hardened, photomicrographs, 875, 876, 877, 879.
hardening: cause, 837, 1138.
colloid factor, 905.
essential points, 1145.
strains, influence, 870.

- Steel: hardening: theories: 902, 1145.
 questionnaire, 860.
 answers, 884.
 conclusions, 872.
 summary, 872, 881.
 see also *Austenite*; *Martensite*; *Pearlite*;
 Slip interference.
 high-speed: effect of carbon in: 1004.
 photomicrographs, 1004, 1005.
 hardness, diagram, 1005.
 rimmed: definition, 1026.
 see also *Rimmed steel*.
 photomicrograph, 946.
 transformations, discussion, 1008.
 ultra-violet ray: photomicrographs, 917-923.
 selective characteristics, 924.
- Steel and iron: committees, xiii.
 papers, list, xviii, xxvi.
- Steel bath, during run, analyses, 1098.
- Steel ingots, basic open-hearth, concentration changes, curves, 1092.
- Steel manufacture committee, xiii.
- STEVENS, B.: *Discussion on Effect of Cyanogen Compounds on Floatability of Pure Sulfide Minerals*, 370-371.
- STEVENS, C. R.: *Discussion on The Effect of Lead and Tin with Oxygen on the Conductivity and Ductility of Copper*, 696-697.
- Stone-sawing sand: photomicrograph, 444.
 properties and uses, 442.
- Stony Point granite: see *Granite*.
- Storage tracks, Magna plant, description, 212.
- Stoughton, Bradley: *Discussion on Effect of Air Gap in Explosion System on Production of Neumann Bands*, 964.
 on hardening of steel, 864, 866, 869, 872, 901.
- STOUGHTON, BRADLEY and MIYAKE, M.: *Preliminary Study of Magnesium-base Alloys*, xxv.
- Strains: see *Steel, hardness*.
- Stress theories, steel hardening, 1145.
- Stripping, electrodes, Nichols series process, 137.
- Strontium, crystal, ion-electron lattice, 649, 650.
- STYRI, H.: *Discussion on Chemical Equilibrium of Manganese, Carbon and Phosphorus in the Basic Open-hearth Process*, 1133-1134.
- Sub-carbide theory, steel hardening, 1145.
- Subsidence Around a Salt Well* (YOUNG), xxvii.
- Subsidence papers, list, xxvii.
- Suckow, discovery well, borate deposits, log, 456.
- SUCKOW, J. K., borate discoveries by, 453.
- Suckow shaft No. 2, borate deposits, log, 458.
- Suggested Nomenclature and Correlation of the Geological Formations in Venezuela* (GARNER), xxiv.
- Sulfates: silver leaching: content, control, 327.
 effect: curves, 324, 325.
 data, 326.
- Sulfides, pure: see *Cyanide solutions, flotation tests*;
 Zinc cyanide; *Zinc sulfates*.
- Sulfur: effect in high-sino slags, 28.
 lead ore, prerostasting, elimination, 175.
- Sulfur: open-hearth: charge, decrease during run, curves, 1080, 1085.
 furnace, during heat, 1093.
 slag, variation, 1082, 1087.
 in refined copper: determination, description, 789, 796.
 relation to heating temperature, 790.
- Sulfur dioxide: in baghouse gas, neutralization, 181.
 partial pressure, 88.
 solubility, discussion, 88.
- Sulfur dioxide and air, ferric sulfate from, experiments, 85-86, 98, 103.
- Sulfur dioxide roaster gas: see *Ferric sulfate and sulfuric acid, from roaster gas*.
- Sulfuric acid: electrolytes, effect on conductivity, 120.
 use in silver leaching, amount, 324.
 see also *Ferric sulfate and sulfuric acid, from roaster gas*.
- SWEETSER, R. H.: *Evaluation of Coal*, xxvii.
- Sykes, W. P.: *Iron-tungsten System*, xxvi, 968, 1008.
 Discussion on Iron Tungsten System, 1004.
- Sylvania standstone, glass sand from, photomicrograph, 412.
- Symons disk crusher, use, 332.
- Symposium: coal and coke, xxvii.
 gas in copper, 742.
 petroleum, xxii, xxiii.
 Salt Creek Field, xix.
- Syracuse, N. Y., meeting, xx.

T

- TAGGART, A. F.: *Discussions on: Classification in Witwatersrand Mills*, 251.
 Investigation of Crushing Phenomena, 313-315.
- Tailings, Midvale, Utah: content, 248.
 disposal, 248.
 see also *Copper tailings*.
- Tanks: electrolytic: copper refining, 130.
 flat-bulb light, 136.
 see also *Electrolyte tanks*; *Leaching tanks*.
- Tapping slag: see *Slag*.
- Taxation and the Oil Industry* (BROKAW), xxii.
- Technologic Progress in the Oil Industry* (FOHS), xxiii.
- Temperature: effect on open-hearth equilibrium, volatilization of lead and silver, 210-211.
 1116, 1124, 1128.
 see also *Austenite, transformation*; *Carbide, in steel, precipitation*; *Ferrous slags, formation*; *Fusion temperatures*; *Iron*; *Iron-tungsten alloys*; *Metalloids*; *Quenching*.
- Tension modulus: Al-Cu-Si alloy, 469.
 data, 476-478.
- Tension tests: Al-Cu-Si alloy, 467.
 data, 476-478.
- Tensional stress, calculation, formula, 843.
- Texas, Outside Gulf Coast (Petroleum Production)* (LAHRE), xxiv.
- Theoretical Rating Compared with Operating Performance of Centrifugal Mine-ventilating Fans* (RICHARDSON), xxiv,

- Thermodynamics, alkali-halide crystals, formulae, 645-646.
- Thickener: see *Genier thickener*; *Gravity thickener*.
- Thigh plate, structure, photomicrograph, 1153.
- THOMPSON, F. C., on hardening of steel, 863, 866, 869, 872, 901.
- THUM, E. E.: *Discussion on Amorphous Cement and the Formation of Ferrite in the Light of X-ray Evidence*, 857-858.
- Tin: effect in: brasses, 807.
copper, 685.
- Tin alloys: see *Copper tin*; *Copper-zinc-tin. tin alloys*.
- Tin and lead, in copper, effect, 680, 687.
- Tin and nickel: see *Aluminum brass*.
- Tin-antimony-lead alloys: see *Lead-antimony*.
- Tin cuttings, precipitating lead, 320.
- Tinguaite, sining tests with, 310.
- Tintic mining district, ore problems, 200.
- Tintic Standard Co.'s Mill* (ALLEN and MADGE), xviii.
- Tintic Standard Mine* (WADE), xviii.
- Tintic Standard mines, A. I. M. E. trip, xvii.
- TOBELMANN, H. A.: *Discussion on Leaching Mixed Copper Ores with Ferric Sulfate, Inspiration Copper Co.*, 74.
- Tolerances: see *Glass sands*.
- Tompkins, Dr. H. Kneebone, work of, 907.
- Tooele, Utah, blowing lead-copper matte, 197.
- Top Slicing in Old Fills at El Bordo Mine, Mexico*, (MECHIN), xxvii.
- Torsion tests: Al-Cu-Si alloy: 468.
data, 476-478.
- "Tough-pitch" copper versus oxygen-free copper, use, 742.
- Tower acid, leaching, comparative cheapness, 79.
- Transmitting tube, leads, embrittlement, causes, 748.
- Transportation, industrial sands, 437.
- Transportation of Petroleum* (FITZGERALD), xxiii.
- Transvaal: see *Geduld Proprietary Mines*; *Springs Mines*; *Witwatersrand*.
- Treating (Oil Refining Processes)* (MILLER), xxiii.
- Treatment of the Telluride-bearing Gold Ores of the Wright-Hargreaves Mines, Ltd.* (MUELLER, GRANT and HEATH), xxv.
- Trend of Prices in the Petroleum Industry* (POGUE), xxiv.
- Troostite: constitution, 1147.
examples, photomicrographs, 1149, 1150.
hardness, cause, 1145.
in iron, condition, 878.
in martensite, photomicrograph, 946.
ultra-violet light: selective characteristics, 924.
photomicrographs, 917, 918.
- Tubes: see *Admiralty tubes*; *Boiler tubes*.
- TUCKER, E. L. and HEAD, R. E.: *Effect of Cyanogen Compounds on Floatability of Pure Sulfide Minerals*, xix, 354-370.
- TUCKER, E. L., GATES, J. F., and HEAD, R. E.: *Effect of Cyanogen Compounds on the Floatability of Pure Sulfide Minerals—II*: xix, 372-380.
- Tungsten: see *Iron-tungsten alloys*; *Iron-tungsten carbon alloys*; *Iron-tungsten system*.
- Turbadium bronze, analysis, 800.
- Turbistone bronze, analysis, 800.
- TURNBULL, GEORGE: *Appalachian Field (Petroleum Production)*, xxiv.
- Twenty-five Years of Metallurgy* (CAMPBELL), xxvii, 1135-1178.
- Twinning theory, steel hardening, 1145.
- Tube mills: description and use, 346.
feed and products, analyses, 346.
- U
- Ulexite: deposits, placer formation, 462.
formation of colemanite from, 450-452.
- Ultra-violet light, selective characteristics, 924.
- Ultra-violet metallography: see *Metallography*.
- UMPLEBY, J. B.: *Increasing the Extraction of Oil by Water Flooding*, xxiii.
- Uncommon metals, reduction and refining, xii.
- United States, zinc production, fluctuation, 6.
- United States Air Service, specifications, heat-treating, Al-Cu-Si alloy, 466.
- United States Borax Co., control of borax lands, 453.
- United States Navy specifications, aluminum-silicon alloys, 619.
see also *Naval brass*.
- United States Smelting Lead Refinery, Inc., electrolyte tests, see *Electrolytes, gold and silver separation*.
- United States Smelting, Refining & Mining Co.: A. I. M. E. trip, xvii.
see also *Midvale, Utah, mill*.
- University of Utah: leaching of copper concentrate tailings, tests, 55.
water-solubility tests, copper ore, 42.
- UREN, L. C.: *Problems of Pumping Deep Wells*, xix.
- Use of Gas Meters for Determination of Pay Strata in Oil Sands* (MILLIKAN), xix.
- Use of Pulverized Coal in Copper Refining Furnaces* (MILLER and BARDWELL), xviii.
- Use of Pulverized Fuel* (SAVAGE), xviii.
- Use of Standard Tests of Molding Sands* (RIE), xxv, 394; Discussion, 397-398.
- Utah: A. I. M. E. field trips, xvii.
lead smelting in, practice, 171-199.
salt for roasting, source, 322.
see also *Bingham*; *Eureka*; *Ironton*; *Lark*; *Midvale*; *Murray*; *Ohio Copper Co. mine*; *Park City*; *Salt Lake City*; *Tooele*.
- Utah Copper Co.: A. I. M. E. trip, xvii.
crushing costs, 340.
see also *Magna plant*.
- Utah parks, A. I. M. E. trips, xviii.
- V
- Vacuum, in filtration, discussion, 227, 234-235.
- VAN ARSDALE, G. D.: *Leaching Mixed Copper Ores with Ferric Sulfate, Inspiration Copper Co.*, xxv, 58-74.
- Discussions on: Leaching Mixed Copper Ores with Ferric Sulfate, Inspiration Copper Co.*, 79, 81, 83.
- Production of Ferric Sulfate and Sulfuric Acid from Roaster Gas*, 98.

- VAN FLEET, H. V. and O'NEILL, F. W.: *Liquid Oxygen as an Explosive*, xxvii.
- VANICK, J. S.: *Discussions on: Effect on Air Gap in Explosion System on Production of Neumann Bands*, 966.
Making Rimmed Steel, 1036.
Microscopic Structure of Copper, 739-740.
- Van't Hoff isochore, formula, 1108.
- VARLEY, T.: *Discussions on: Chief Consolidated Volatilization Process and Mill*, 209.
Chloridizing Mill of the Standard Reduction Co., 338.
- Ventilation, lead blast-furnace tapping-floor, 188.
- Venezuela and the West Indies (Petroleum Production) (HOPKINS and WASSON), xxiv.
- Virginia: bentonite, source, 390.
quartzite, occurrence, 422.
- Viscosity, ferrous slags, 16.
- Volatilization: see *Chief Consolidated process; Chloride Volatilization; Lead, Oxide Volatilization*.
- Volatilization loss, furnaces, prevention, 340.
- Voltage: see *Electrolysis; Electrolyte*.
- Voltage drop, electrolytes, effect of ammonia, 112.
- Von Juptner, —, on oxide slags in iron alloys, 1110.
- V
- WADE, J. W.: *Tintic Standard Mine*, xviii.
- WALKER, A. L.: *Development of Multiple-series Tank*, 124.
Discussions on: Effect of Zinc Oxide on the Formation Temperature of Some Ferrous Slags, 30.
Improvements in the Series System of Electrolytic Copper Refining Recently Developed by the Nichols Copper Co., 143-144.
- Warm Spring Ridge, glass-sand quarry, 415.
- WARNER, D. M. and DANIELS, SAMUEL: *Mechanical Properties of the Aluminum-copper-silicon Alloy as Sand Cast and as Hand Treated*, xx, 464-478.
- WARTMAN, F. S., OLDRIGHT, G. L., KEYES, H. E. and: *Production of Ferric Sulfate and Sulfuric Acid from Roaster Gas*, xix, 84-98.
- Washers, glass sands, view, 414.
- Washing: anodes, Sperry process, 167.
industrial sands, 436.
see also *Gravel; Sand*.
- Washing method, leaching tests, 68.
- Washing and Sizing Sand and Gravel (SHAW), xxv, 424-433.
- Washington: see *Northport*.
- WASSON, H. J. and HOPKINS, E. B.: *Venezuela and the West Indies (Petroleum Production)*, xxiv.
- Water: copper concentrate, removal, 50.
leaching: amount, determination, 37.
see also *Ohio Copper Co. mine*.
percolation, methods, 38-42.
washing sand and gravel, amount needed, 428.
see also *Bingham mines; Film water*.
- Water jackets, lead smelting, first use, 171.
- Water Shut-off Methods in Salt Creek Field* (ARMSTRONG and RADER), xix.
- Water supply: see *Standard Reduction Co. mill*.
- Waters of Salt Creek Field (YOUNG and ESTABROOK), xix.
- WATTS, A. C.: *Electric Shot-firing in Coal Mines*, xviii.
- Wax Separation (MILLER), xxiii.
- Wear tests: see *Pebble mills; Quartz*.
- Wedge roaster: lead ore: description, 174.
operation, 174-177.
- WEIGEL, W. M.: *Preparation and Use of Industrial Special Sands*, xxv, 434-447.
Discussions on: Mining and Preparation of Eastern Molding Sands, 388, 391.
Preparation and Use of Industrial Special Sands, xxv, 448.
Standard Tests of Molding Sands, 397.
- Weight: see substances named.
- WELLING, L. H.: *Jenkins Process*, xxiii.
- WELLS, A. E.: *Comparative Value as Motor Fuel of Cracked Gasoline vs. Straight Run Gasoline*, xxiii.
- Wertz oil and gas field, A. I. M. E. trip, xvii.
- West Virginia: glass sands, occurrence, mining and preparation, 415-420
industrial sands, occurrence, 434.
- Wet crushing: see *Crushing, wet*.
- WHETSEL, R. V. and GARFIAS, V. R.: *Mexican Oil Fields*, xxiv.
- WHITE, L. H.: *Possibilities of Future Production from the Pre-Chattanooga Series of Northeastern Oklahoma*, xxiv.
- WHITEHEAD, E. and JONES, E. O.: *Annealing Cracking of the Nickel Silvers*, xx, 834-849.
- Whitley's basicity index, formula, 1111.
- WIGGINS, J. H.: *Evaporation Loss in Transportation of Petroleum*, xxiii.
- WIGTON, G. H.: *Chief Consolidated Volatilization Process and Mill*, xix, 200-209.
- WILDER, F. A.: *Discussion on American Glass Sands, Their Properties and Preparations*, 422.
- WILSON, J. H. and BARTRAM, J. G.: *Core Drilling in Geologic Exploration as Applied in Wyoming and Montana*, xix.
- Winnamuck mine, Utah, water jacket used in lead smelting, 171.
- Wire-bar furnace, for copper cathodes, practice, 138-140.
- WITHERELL, C. S.: *Discussions on: Effect of Lead and Tin with Oxygen on the Conductivity and Ductility of Copper*, 695.
Effect of Zinc Oxide on the Formation Temperature of Some Ferrous Slags, 28-30.
Ezudations on Copper Castings, 706.
Hardness of Copper and Meyer's Analysis, 671-674, 675, 677.
Leaching Mixed Copper Ores with Ferric Sulfate, Inspiration Copper Co., 80.
- Witwatersrand: gold ore, grinding, size, 250.
mills: classification in: description, 239, 247.
discussion, 247.
- WOOD, F. E.: *Rocky Mountain District (Petroleum Production)*, xxiv.

- WOODWARD, A. H.: *Discussion on Making Rimmed Steel*, 1044.
- WORK, L. T.: *Discussions on: Investigation of Crushing Phenomena*, 316.
Mechanism of Filtration, 234, 235.
- WORK, L. T., HIXON, A. W., ODELL, I. H. and: *Mechanism of Filtration*, xxv, 225-234.
- World Production of Petroleum in 1925 (DE GOLYER), xxii.
- WRIGHT, FAY: *Some Economic Aspects of the Community Oil Lease*, xxiv.
- Wrist-piece, ancient structure, photomicrograph, 1152.
- Wrought iron: intercrystalline brittleness, photomicrographs, 751.
Neumann bands in, 1140.
- Wyoming, bentonite, use, 389.
see also *Casperr*; *Rawlins*.
- X-ray: anode, water-cooled, leaks in, causes, 746.
microstructures of crystals, 850.
- YANCY, H. F. and FRASER, THOMAS: *Air Sand Process of Cleaning Coal*, xxvii.
- YAP, C. P.: *Discussion on Effect on Air Gap in Explosion System on Production of Neumann Bands*, 965.
- Yellowstone Park, A. I. M. E. trip, xviii.
- YOUNG, C. M.: *Subsidence Around a Salt Well*, xxvii.
- YOUNG, H. W. and ESTABROOK, E. L.: *Waters of Salt Creek Field*, xix.
- ZAVOICO, B. B.: *Russia (Petroleum Production)*, xxiv.
- ZICKRICK, LYALL: *Discussion on Lead Antimony System and Hardening of Lead Alloys*, xxv, 529-535.
- ZICKRICK, LYALL, DEAN, R. S., NIX, F. C., and: *Lead Antimony System and Hardening of Lead Alloys*, xxv, 505-529.
- Zinc: concentrating recoveries, 351.
flotation, oils and reagents, 353.
production, U. S., fluctuations, reasons, 5, 6.
reduction and refining, committee, xii.
- Zinc alloys: see *Copper-zinc*; *Copper-zinc-tin*; and brasses named.
- Zinc cyanide: effect on pure sulfides: discussion, 365, 375.
photomicrographs, 365-369, 377-379.
flotation of sulfides, effect, 357.
- Zinc oxide: ferrous slags: content, 19-27.
effect on formation temperature, 3-30.
replacing lime, iron oxide and silica, slag-formation temperatures, 13-17.
- Zinc sulfate, flotation of sulfides, effect, 358-361.
- Zincate, slag, zinc-carrying ingredient, 29.

P
4087

